Student's Intensifier

II PUC Chemistry Short Notes for PU Board Examination-2024

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RAVERSK

Important Questions:

Derivation of integrated rate equation for zero order reaction:

Or

Derive an expression of rate constant for zero order reaction:

Consider a zero reaction, $R \rightarrow P$

According to rate law,

Rate = k [R]⁰
-
$$\frac{d[R]}{dt} = k$$

Integrate both sides

$$\int d[R] = -k \int dt$$

d[R] = -k dt

 $[R] = -k t + I \rightarrow (1)$

At time t = 0, $[R] = [R]_o$

 $[\mathbf{R}]_{0}$ is the initial concentration of reactant.

'I' is the integration constant.

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Therefore, [R]_0 = I substitute in equation (1)
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$$\therefore \quad [\mathbf{R}] = -\mathbf{k} \, \mathbf{t} \, + [\mathbf{R}]_0$$

$$\mathbf{k} = \frac{[\mathbf{R}]_0 - [\mathbf{R}]}{\mathbf{t}}$$

Derivation of integrated rate equation for first order reaction:OrDerive an expression of rate constant for first order reaction:Consider a first order reactionR \rightarrow Products(R is reactant)

According to the rate law,

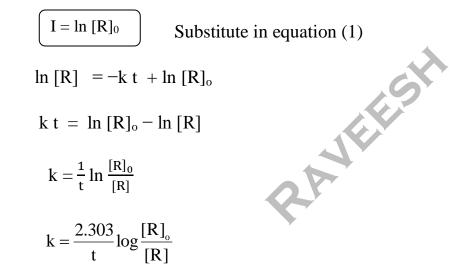
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Rate = k[R]¹ $-\frac{d[R]}{dt} = k[R]$ 'k' is rate constant or velocity constant. $\frac{d[R]}{[R]} = -k dt$

Integrating both sides

$$\int \frac{d[R]}{[R]} = -k \int dt$$
$$\ln [R] = -k t + I \rightarrow (1)$$

At time t = 0, $[R] = [R]_0$ $[R]_0$ is the initial concentration of reactant.



Manufacture of potassium dichromate from chromite ore:

Chromite ore – FeO.Cr₂O₃ (or) FeCr₂O₄ $4FeCr_2O_4 + 8Na_2CO_3 + 7O_2 \rightarrow 8Na_2CrO_4 + 2Fe_2O_3 + 8CO_2$ Sodium chromate $2Na_2CrO_4 + 2H^+ \rightarrow Na_2Cr_2O_7 + 2Na^+ + H_2O$ Sodium dichromate $Na_2Cr_2O_7 + 2KC1 \rightarrow K_2Cr_2O_7 + 2NaC1$ Potassium dichromate

Manufacture of potassium Permanganate Pyrolusite (MnO₂):

 $2MnO_2 + 4KOH + O_2 \rightarrow 2K_2MnO_4 + 2H_2O$

Potassium manganate

$$3MnO_4^{2-} + 4H^+ \rightarrow 2MnO_4^- + MnO_2 + 2H_2O$$

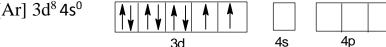
Permanganate Manganate

Applications of VBT:

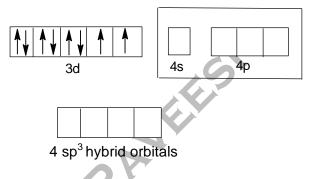
1) [NiCl₄]⁻² [tetrachloridonickelate (II) ion] :

Oxidation state of Ni = +2,

 $Ni^{+2} - [Ar] 3d^8 4s^0$



Cl⁻ is weak ligand, unpaired electrons do not pair up.



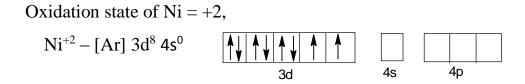
Four sp³ hybrid orbitals filled by electrons donated by 4 Cl⁻ ligands.

Hybridization - sp³

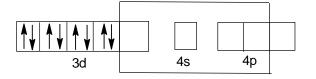
Geometry – Tetrahedral

Magnetic nature: Paramagnetic (Due to presence of two unpaired electrons)

2) Ni(CN)₄]⁻² [tetracyanidonickelate (II) ion]:



CN⁻ strong ligand, unpaired electrons get paired.





4 dsp² hybrid orbitals

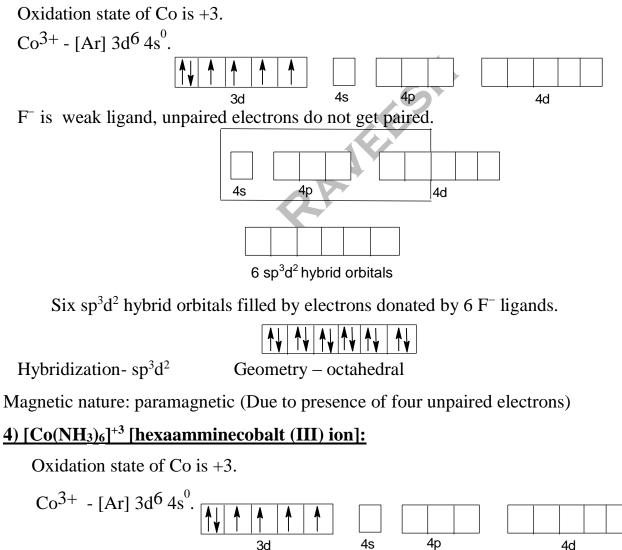
Four dsp² hybrid orbitals filled by electrons donated by 4 CN⁻ ligands.

$\left[\begin{array}{c} \uparrow \downarrow \\ \uparrow \downarrow \\ \end{array} \right] \left[\begin{array}{c} \uparrow \downarrow \\ \uparrow \downarrow \\ \end{array} \right] \left[\begin{array}{c} \uparrow \downarrow \\ \uparrow \downarrow \\ \end{array} \right] \left[\begin{array}{c} \uparrow \downarrow \\ \uparrow \downarrow \\ \end{array} \right] \left[\begin{array}{c} \uparrow \downarrow \\ \uparrow \downarrow \\ \end{array} \right]$

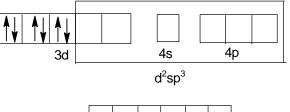
Hybridization- dsp² Geometry – Square planar

Magnetic nature: Diamagnetic (Due to absence of unpaired electrons)

3) [CoF₆]⁻³ [hexafluoridocobaltate (III) ion]:



NH₃ is strong ligand, unpaired electrons get paired.



6 d²sp³ hybrid orbitals

Six $d^2 sp^3$ hybrid orbitals filled by electrons donated by 6 NH₃ ligands.

| ↑↓ ↑ ↓ | ↑ ↓ | ≜ ↓ | ₽ | A ↓ |
|---------------|------------|------------|---|------------|
|---------------|------------|------------|---|------------|

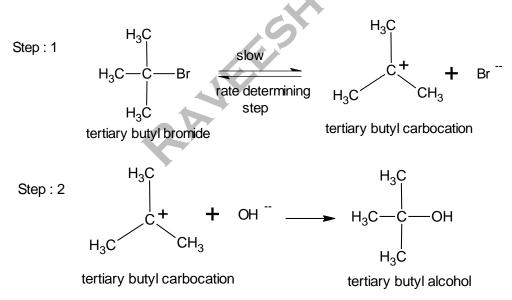
 $Hybridization-\ d^2sp^3 \qquad \qquad Geometry-\ Octahedral$

Magnetic nature: Diamagnetic (Due to absence of unpaired electrons)

$\underline{S_N}^1$ reaction (Substitution nucleophilic first order reaction):

Ex: Hydrolysis of tertiary butyl bromide with aqueous NaOH gives tertiary butyl alcohol.

Mechanism:



Rate \propto [alkyl halide], hence S_N^1 reaction is first order reaction.

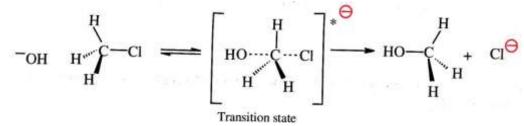
Rate = k[alkyl halide]

$\underline{S_N}^2$ reaction (Substitution nucleophilic second order reaction):

Ex: Hydrolysis of methyl chloride with aqueous NaOH gives methyl alcohol.

Mechanism: The nucleophile (OH⁻) attacks the carbon from the back side of the leaving group

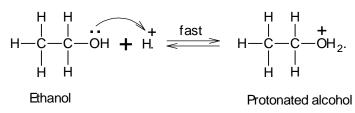
(Cl⁻) and form transition state. The Cl⁻ is completely removed to give the product (methyl alcohol) with inversion of configuration.

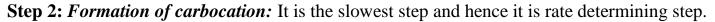


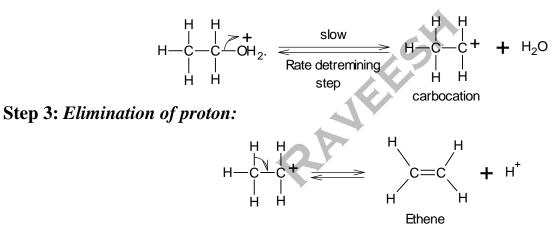
Rate \propto [alkyl halide] [OH⁻], hence S_N² reaction is second order reaction. Rate = k[alkyl halide] [OH⁻],

Mechanism of dehydration of ethanol to ethene:

Step 1: Protonation of alcohol:

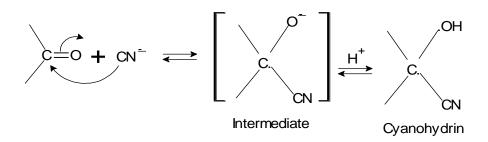






Mechanism of addition of HCN to aldehydes or ketones:

HCN + OH
$$\stackrel{-}{\longrightarrow}$$
 CN $\stackrel{-}{\longrightarrow}$ HCN + H₂O



Chapter wise Important Questions:

Unit-01: Solutions

Binary solution: A solution which contains only two components is called a binary solution.

Saturated solution: A solution in which no more solute can be dissolved at the same temperature and pressure.

Molarity (M):

Molarity: "Number of moles of the solute dissolved in one liter of the solution".

- ✤ Molarity is temperature dependent.
- ✤ Molarity of a solution decreases with the increase in temperature

Molality: "Number of moles of the solute dissolved in one kg (1000g) of the solvent".

✤ Molality is a temperature independent quantity.

Factors that influence solubility of gases in liquids:

Temperature: Solubility of gas in liquid decreases with the increase in temperature (Because solubility of gas in a liquid is *exothermic*)

Pressure: The solubility of a gas in a liquid increases with the increase in pressure.

Henry's law:

"The partial pressure of gas in vapour phase is directly proportional to the mole fraction of gas in the solution".

| i.e., | $p \propto x$ | $p \rightarrow partial pressure of the gas.$ | |
|-------|-----------------|--|---|
| | $p=K_H\times x$ | $x \rightarrow$ solubility in mole fraction. | $K_{\rm H} \rightarrow$ Henry's constant. |
| | | | |

"Higher the value of K_{H} , lower the solubility of gas".

Applications of Henry's law:

1) To increase the solubility of carbon dioxide in soda bottle and soft drinks bottles are sealed under high pressure of CO₂.

2) Oxygen cylinders carried by sea divers are filled with air which is diluted with helium to avoid the risk of bends.

Raoult's law for liquid-liquid solution:

"For a solution of volatile liquids, the partial vapour pressure of each component of solution is directly proportional to its mole fraction in the solution".

Differences between

| Ideal solutions | Non-ideal solutions | |
|-----------------------------------|-----------------------------------|--|
| 1. Obey Raoult's law at all | Does not obey Raoult's law at all | |
| concentration. | concentration. | |
| 2. $\Delta H_{\text{mixing}} = 0$ | $\Delta H_{mixing} \neq 0$ | |
| 3. $\Delta V_{\text{mixing}} = 0$ | $\Delta V_{mixing} \neq 0$ | |

Examples ideal solutions: Benzene + Toluene, n-hexane + n-heptane

Examples non-ideal solutions: Acetone + Ethanol

Acetone + CS₂

Acetone + Chloroform Phenol + Aniline

Differences between

| Non-ideal solution shows positive | Non-ideal solution shows negative | |
|-----------------------------------|-----------------------------------|--|
| deviation from Raoult's law | deviation from Raoult's law | |
| 1. $\Delta H_{mixing} > 0$ | 1. $\Delta H_{\text{mixing}} < 0$ | |
| 2. $\Delta V_{\text{mixing}} > 0$ | 2. $\Delta V_{\text{mixing}} < 0$ | |

Deviation shown by some binary solutions:

| Non-ideal solutions | | Type of deviation from Raoult's law | |
|---------------------|--|-------------------------------------|--|
| 1. | Acetone + Ethanol | Positive deviation | |
| 2. | Acetone + Carbon disulphide (CS ₂) | Positive deviation | |
| 3. | Acetone + Chloroform | Negative deviation | |
| 4. | Phenol + Aniline | Negative deviation | |

Azeotropes or Azeotropic mixture: "Binary mixtures having the same composition in liquid and vapour phase and boil at a constant temperature"

a) Minimum boiling azeotropes: The solutions which show a large positive deviation from Raoult's law form minimum boiling azeotrope. *Ex:* 95% ethanol + 5% H_2O by volume

b) Maximum boiling azeotropes: The solutions which show a large negative deviation from Raoult's law form maximum boiling azeotrope. Ex: 68% nitric acid and 32% water by mass
Osmosis: The spontaneous movement of solvent molecules from solution of lower concentration to solution of higher concentration through semipermeable membrane is called osmosis.

<u>Semipermeable membrane</u>: The membrane which allows the solvent molecules to pass through it but not solute particles is called semipermeable membrane.

✓ 0.9% (w/v) NaCl in water is called *normal saline solution*.

Osmotic pressure:

"The pressure to be applied on the solution of higher concentration just to stop osmosis".

- Isotonic solutions: "Two solutions having same osmotic pressure at a given temperature" are called isotonic solutions.
- <u>Hypertonic solution:</u> "A solution having higher osmotic pressure with respect to other" is called hypertonic solution.
- <u>Hypotonic solution:</u> "The solution having lower osmotic pressure with respect to other" is called hypotonic solution.

| When blood cells are placed in solution containing more | Shrinks (size of blood cells |
|---|------------------------------|
| than 0.9% (mass/volume) sodium chloride. | decreases) |
| When blood cells are placed in solution containing less | swell(size of blood cells |
| than 0.9% (mass/volume) sodium chloride. | increases) |
| When blood cells are placed in 0.9% (mass/volume) | Remains same (No change |
| sodium chloride. | in size of blood cells) |

Reverse osmosis: "The process of reversing the direction of osmosis by applying the pressure higher than the osmotic pressure to the solution of higher concentration" is called reverse osmosis.

Application of reverse osmosis: Desalination of sea water.

Van't Hoff's factor (i): Van't Hoff factor defined as;

 $i = \frac{Normal molar mass}{1}$

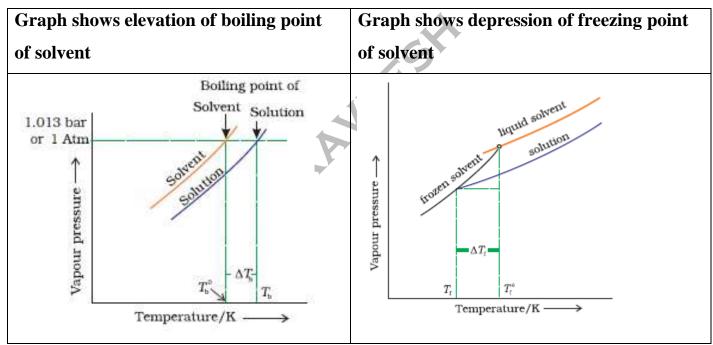
| | Abnormal molar mass |
|-------------------------|--|
| Van't Hoff's factor (i) | Conclusion |
| i = 1(unity) | Neither association nor dissociation of solute |

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| i < 1(unity) | Association of solute |
|--------------|------------------------|
| i > 1(unity) | Dissociation of solute |

Van't Hoff's factor values for different solutions:

| Solution | Van't Hoff's factor (i) |
|------------------------------------|-------------------------|
| Ethanoic acid in benzene | 0.5 |
| Aq.KCl | 2 |
| Aq. NaCl | 2 |
| Aq. MgSO ₄ | 2 |
| Aq. K ₂ SO ₄ | 3 |





 $\frac{\mathbf{P}^0 - \mathbf{P}}{\mathbf{P}^0} = \frac{\mathbf{W}_2}{\mathbf{M}_2} \times \frac{\mathbf{M}_1}{\mathbf{W}_1}$ Relative lowering of vapour pressure (RLVP),

 $p^{o} \rightarrow Vapour pressure of pure solvent$ $p \rightarrow Vapour pressure of solution$



Osmotic pressure, $\pi = \frac{W_2 \times R \times T \times 1000}{M_2 \times V(ml)}$

 $(R = 0.0821 \text{ L atm } \text{K}^{-1} \text{ mol}^{-1} \text{ or } 0.083 \text{ L bar } \text{K}^{-1} \text{ mol}^{-1}), V = \text{volume of solution}$ **Student's Intensifier**

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• Elevation of boiling point, $\Delta T_{b} = T_{b} - T_{b}^{0} = \frac{K_{b} \times W_{2} \times 1000}{M_{2} \times W_{1}}$

 T_b^0 be the freeing point of the pure solvent and T_b be the freezing point of the solution.

' K_b ' is the boiling point elevation constant or molal elevation constant or Ebullioscopy constant.

• Depression in freezing point,
$$\Delta T_f = T_f^0 - T_f = \frac{K_f \times W_2 \times 1000}{M_2 \times W_1}$$

 T_{f}^{0} be the freeing point of the pure solvent and T_{f} be the freezing point of the solution.

 ${}^{^{\prime}}K_{b}{}^{^{\prime}}$ is the freezing point depression constant or molal depression constant or Cryoscopic constant.

 $W_2 \rightarrow$ mass of the solute $M_2 \rightarrow$ molar mass of the solute $w_1 \rightarrow$ mass of the solvent



Unit-02: Electrochemistry

Differences between

| | Metallic/Electronic Conductors | | Ionic/ Electrolytic conductors | |
|---|--|---|---|--|
| * | Conduct electricity due to movement | * | Conduct electricity due to movement of | |
| | of electrons. | | ions. | |
| * | Conduction takes place in solid state. | * | Conduction takes place in molten state/ | |
| | | | in aqueous solutions. | |
| * | Metallic conductance decreases with | * | Ionic Conductance increases with | |
| | increase in temperature. | | increases in temperature. | |

Factors affecting the electrolytic or ionic conductance:

- (i) The nature of the electrolyte
- (ii) The concentration of the electrolyte
- (iii) Temperature

Factors affecting the electronic or metallic conductance:

- (i) The number of valence electrons per atom
- (ii) Nature and structure of metal
- (iii) Temperature

<u>Cell constant (G*)</u>: The ratio of the distance between the electrodes (*l*) to the area of cross

section (A) of the electrodes. Cell constant (G*) = $\frac{\ell}{A}$

Specific conductance or conductivity:

"Specific conductance is conductance of $1m^3$ of electrolytic solution". Unit is Sm^{-1}

• On dilution specific conductance (conductivity) decreases. Because on dilution, number of ions per unit volume decreases. Hence specific conductance (conductivity) decreases.

Molar conductance (or) Molar Conductivity:

"Conductivity due to all the ions present in 1 mole of electrolytic solution". Unit is Sm^2mol^{-1}

• On dilution (decrease in concentration), molar conductivity increases.

Kohlrausch's Law of independent migration of ions:

"Limiting molar conductivity of an electrolyte is the sum of the individual contributions of the cation and anion of the electrolyte."

$$\Lambda^{0}{}_{m}(\text{NaCl}) = \lambda^{0}{}_{\text{Na}^{+}} + \lambda^{0}{}_{\text{Cl}^{-}}$$

Applications of Kohlrausch's Law:

1) Calculation of molar conductivity at infinite dilution (Λ^0_m) for weak electrolyte from experimentally determined values of Λ^0_m of suitable strong electrolytes.

2) Determination of degree of dissociation and dissociation constant of weak electrolyte.

Products of electrolysis of some electrolytes:

| Electrolytes | Cathode | Anode |
|-----------------------------|----------------|-----------------|
| Molten NaCl | Na | Cl ₂ |
| Aqueous NaCl | H ₂ | Cl ₂ |
| Dilute sulphuric acid | H ₂ | O ₂ |
| Concentrated sulphuric acid | H ₂ | $S_2O_8^{2-}$ |

Faraday's I law: "During electrolysis, the mass of substance deposited at an electrode is directly proportional to quantity of electric charge passed through the electrolytic solution".

Faraday's II Law: "When the same quantity of electricity passes through solutions of different electrolytes, the masses of different substances deposited at the electrodes are directly proportional to their respective equivalent masses."

Faraday: "The total charge carried by one mole of electrons".

| Reduction or Oxidation | Charge required |
|---|--------------------------|
| One mole Cu ⁺² to Cu or Zn ⁺² to Zn or Mg ⁺² to Mg | 2F (2 x 96500 = 193000C) |
| One mole Al ⁺³ to Al | 3F (3 x 96500 = 289500C) |
| One mole MnO_4^- to Mn | 5F (5 x 96500 = 482500C) |
| One mole H ₂ O to O ₂ | 2F (2 x 96500 = 193000C) |
| One mole FeO to Fe ₂ O ₃ | 1F (96500C) |

Daniel Cell:

A galvanic cell in which the negative electrode is zinc and the positive electrode is copper is called **Daniel cell**.

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Anode : $Zn_{(s)} \rightarrow Zn^{+2}{}_{(aq)} + 2e^{-n}$

Cathode : $Cu^{+2}_{(aq)} + 2e^{-n} \rightarrow Cu_{(s)}$

Overall reaction of Daniel cell is, $Zn_{(s)} + Cu^{+2}_{(aq)} \rightarrow Zn^{+2}_{(aq)} + Cu_{(s)}$

Symbolical representation of Daniel cell is $Zn_{(s)} / Zn^{+2}(_{aq)} / Cu^{+2}_{(aq)} / Cu_{(s)}$

Functioning of Daniel cell when external voltage (E_{ext}) is applied against the cell potential

(or) emf of Daniel cell:

<u>**Case-1**</u>: If $E_{ext} < 1.1V$ E^{-n} flows Zn to Cu and current flows from Cu to Zn.

<u>Case-2</u>: If $E_{ext} > 1.1V$ E^{-n} flows Cu to Zn and current flows from Zn to Cu.

<u>Case-3</u>: If $E_{ext} = 1.1V$ No flow of $e^{-n}s$ and current and no chemical reaction.

Corrosion of iron (Rusting) : Electrochemical phenomenon.

"When the iron is exposed to moist air for long time a brown coating of hydrated ferric oxide formed on surface of iron" this phenomenon is called **Rusting**.

Reactions during rusting of iron:

Anode: $2Fe_{(s)} \rightarrow 2Fe^{2+} + 4e^{-}$

Cathode: $O_{2(g)} + 4H^+_{(aq)} + 4e^- \rightarrow 2H_2O_{(l)}$

Hydrated ferric oxide is called 'rust'. Composition of rust \rightarrow Fe₂O₃. xH₂O

Methods for the prevention of Corrosion:

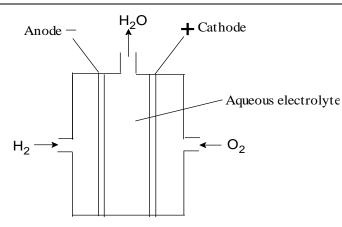
- ✓ Coating the surface of metal by paint (or) oil or some chemicals like bisphenol.
- ✓ Cover the surface of object by other metals like Sn, Zn etc.

Fuel cells:

Fuel cells are galvanic cells which are generate the electrical energy by the combustion of fuels like methane, hydrogen, methanol etc.

Reactions at anode and cathode of H₂ – O₂ fuel cell:

Anode: $2H_{2(g)} + 4OH_{(aq)} \rightarrow 4H_2O_{(l)} + 4e^-$ Cathode: $O_{2(g)} + 2H_2O_{(l)} + 4e^- \rightarrow 4OH_{(aq)}$ <u>Overall reaction:</u> $2H_{2(g)} + O_{2(g)} \rightarrow 2H_2O_{(l)}$ Diagram of $H_2 - O_2$ fuel cell:



Standard hydrogen electrode (SHE) or

- > Standard electro potential (E^0) of H_2 electrode 'Zero'
- ► Electrode reaction \rightarrow $H^{+}_{(aq)}$ + $e^{-n} \rightleftharpoons \frac{1}{2} H_{2(g)}$
- > Symbolically representation of SHE is $Pt(s) / H_{2(g)} / H^+ (aq, 1M)$
- > The pressure of hydrogen gas in SHE is 1 bar.
- > The concentration of hydrogen ion in the solution is 1 molar (1M).

Electrode potential [E]: "A potential difference develops between the electrode and electrolyte" is called electrode potential.

Factors affecting electrode potential:

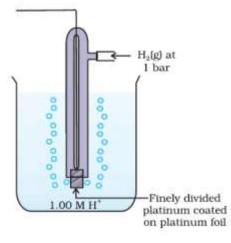
- i) Nature of electrode ii) Nature and Concentration of ions in solution iii) Temperature
- > Nernst equation for Daniel cell, $Zn_{(s)} / Zn^{+2}_{(aq)} / Cu^{+2}_{(aq)} / Cu_{(s)}$ (n = 2)

$$E_{cell} = E_{cell}^{0} - \frac{2.303RT}{2F} \log \frac{[Zn^{+2}]}{[Cu^{+2}]}$$
At 298 K, $E_{cell} = E_{cell}^{0} - \frac{0.0591}{2} \log \frac{[Zn^{+2}]}{[Cu^{+2}]}$

Differences between Emf and Cell potential:

| Emf | Cell potential / Voltage |
|--|---|
| It is the potential difference between the two | It is the difference b/w the electrode |
| electrodes when no current is drawn through | potentials of the two electrodes when the |
| the cell. | cell is under operation. |
| It is measured using potentiometer. | It is measured using voltmeter. |

Electrochemical series (or) Activity series: "The series of arrangement of standard electrodes in increasing order of the standard reduction potential (SRP) values".



Relation between standard cell potential (E^{0}_{Cell}), Gibb's standard free energy change (ΔG^{0})

 $\Delta G^0 = -nFE^0_{cell}$

 $\Delta G^0 \rightarrow$ standard free energy change $F \rightarrow$ Faraday (96500C)

 $n \rightarrow$ number of electrons in redox reaction $E_{cell}^0 \rightarrow$ Standard cell potential

| E ⁰ _{cell} | ΔG^0 | Reaction at standard conditions |
|--------------------------------|--------------|---------------------------------|
| > 0 (+ve) | < 0 (-ve) | Spantaneous |
| < 0 (-ve) | >0 (+ve) | Non-spantaneous |
| = 0 | = 0 | At equilibrium |

Relation between Gibb's standard free energy change (ΔG^0) and equilibrium constant (K_c):

 $\Delta G^0 = -2.303 RT \log K_c$ K_c is equilibrium constant R = 8.314J/mol/K

Relation between standard cell potential (E⁰_{Cell}) and equilibrium constant (K_c): (At 298K)

$$E_{cell}^0 = \frac{0.0591}{n} \log K_c$$
 (n = Number of electrons involved)

G

Summary:

| Kc | Δ G ⁰ | Reaction at standard conditions |
|-----|-------------------------|---------------------------------|
| > 1 | < 0 (-ve) | Spantaneous |
| < 1 | >0 (+ve) | Non-spantaneous |
| 1 | 0 | At equilibrium |

Primary batteries:

 \Rightarrow Primary battery one which become dead over a period of time and cannot be recharged.

Ex: Dry cell (Leclanche cell), Mercury cell.

a) Dry cell (Leclanche cell):

Anode: Zinc

Cathode: A graphite rod which is surrounded by MnO₂ and powdered carbon

Electrolyte: Moist paste of ZnCl₂ and NH₄Cl

Reactions:

At anode: $Zn \rightarrow Zn^{+2} + 2e^{-n}$

At cathode: $2MnO_2 + 2NH_4^+ + 2e^{-n} \rightarrow 2MnO (OH) + 2NH_3$

b) Mercury cell:

Anode: Zinc-amalgam (Zn-Hg)

Cathode: Mercury oxid (HgO) and carbon

Electrolyte: KOH + ZnO

<u>Reactions:</u> At anode: $Zn (Hg) + 2\overline{O}H \rightarrow ZnO_{(s)} + H_2O + 2e^{-n}$

At cathode: HgO_(s) + H₂O_(l) + $2e^{-n} \rightarrow$ Hg_(l) + $2\overline{O}H$

 \Rightarrow The cell potential of mercury cell is remains constant throughout its life.

 \Rightarrow It is suitable for low current devices like hearing aids.

2) <u>Secondary batteries</u>: Rechargeable batteries are called as secondary batteries.

Ex: Lead storage cell, Nickel-cadmium cell

Lead storage cell or battery:

| Anode | <u>:</u> Pb | Cathode: PbO ₂ | Electrolyte: 38 % H ₂ SO ₄ |
|----------|------------------|--------------------------------------|--|
| Reaction | <u>s:</u> | | |
| Anode: | $Pb(s) + SO_4^2$ | $-(aq) \rightarrow PbSO_4(s) + 2e^-$ | 19 |
| Cathode: | $PbO_2(s) + SC$ | $4^{2-}(aq) + 4H^{+}(aq) + 2e^{-} -$ | $\Rightarrow PbSO_4(s) + 2H_2O(l)$ |
| | | *** | ** |
| | | | |

Unit-03: Chemical Kinetics

Rate of chemical reaction: The change in molar concentration of reactants or products in unit time.

The units for the rate of reaction are **mol** $L^{-1} s^{-1}$

The units for the rate of gaseous reaction are $atm s^{-1}$

Average rate: The rate of a reaction measured over a long interval of time.

Instantaneous rate: The change in molar concentration of either reactants or products in extremely small interval of time.

Factors affecting the rate of reaction:

a) Molar concentration of reactants b) Temperature c) Catalyst d) Intensity of light

Rate law (law of mass action):

It states that "at constant temperature, rate of a reaction is directly proportional to product of the molar concentration of reactants and each concentration term is raised to suitable powers which may or may not be same as the stoichiometric coefficients of reactants in balanced chemical equation".

<u>Rate expression or Rate equation:</u> It is an equation that relates the rate of the reaction and molar concentration of reactants.

<u>Order of reaction</u>: It is the sum of the powers of concentration of reactants in an experimentally determined rate equation.

Molecularity: "The number of reacting species (molecules, atoms or ions) taking part in an

elementary reaction or in a rate determining step of a complex reaction which collide

simultaneously to bring about a chemical reaction".

Examples: $NH_4NO_2 \rightarrow N_2 + 2H_2O$ (Molecularity = 1)

 $2HI \rightarrow H_2 + I_2$ (Molecularity = 2)

 $2NO + O_2 \rightarrow 2NO_2$ (Molecularity = 3)

Units of rate constant:

| Order of reaction | Units of rate constant: |
|-----------------------|---|
| n th order | $\operatorname{mol}^{1-n} \operatorname{L}^{n-1} \operatorname{sec}^{-1}$ |
| Zero order | $mol L^{-1} sec^{-1}$ |

| 1 st order | sec ⁻¹ |
|-----------------------|---------------------------------------|
| 2 st order | $L \text{ mol}^{-1} \text{ sec}^{-1}$ |

Differences between order and molecularity:

| Order | Molecularity |
|---|---|
| It is the sum of powers of the | It is the number of molecules of reactants |
| concentration terms in the rate law | taking part in an elementary reaction or in a |
| expressions. | rate determining step of a complex reaction. |
| It is an experimental value | It is a theoretical value |
| Order can be zero or fraction | Molecularity cannot be zero or non-integer |
| Order is applicable to elementary as well | Molecularity applicable only for elementary |
| as complex reactions | reactions |

Zero order reaction: The reaction in which rate of reaction is independent of concentration of all the reactants".

Example: Decomposition of NH₃ on platinum surface. $2NH_3 \xrightarrow{hot, Pt} N_2 + 3H_2$

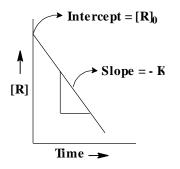
Decomposition of HI on gold surface. 2HI $\xrightarrow{\text{hot, Au}}$ H₂ + I₂

In zero order reaction,

- \blacktriangleright The rate of the reaction is equal to the rate constant (k) of that reaction.
- ➤ Units of rate is same as that of rate constant.

<u>Graph:</u> $[R] = -k t + [R]_0$ is in y = m x + c (straight line equation) form.

When we plot the graph of '[R]' v/s 't' straight line with a slope (m) = -k and intercept (c) = [R]₀.



First order reaction: "The reaction in which rate of reaction is directly proportional to first power of molar concentration of reactants".

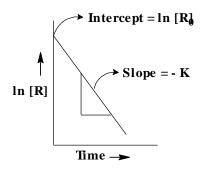
Examples: Hydrogenation of ethene. $C_2H_4 + H_2 \rightarrow C_2H_6$

All natural and artificial radioactive disintegrations

Decomposition of N₂O and N₂O₅

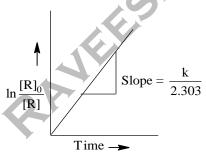
Thermal decomposition of hydrogen peroxide.

<u>**Graphs:**</u> i) $\ln [R] = -k t + \ln [R]_0$ is in y = m x + c (straight line equation) form. When we plot the graph of 'ln [R]' v/s 't' straight line with a slope (m) = -k and intercept (c) = ln [R]_0.



ii) $\log \frac{[R]_0}{[R]} = \frac{kt}{2.303}$ is also in y = m x + c (straight line equation) form. When we plot the graph of

$$\log \frac{[R]_0}{[R]}$$
 v/s't' straight line with a slope (m) = $\frac{k}{2.303}$ and intercept (c) = 0.



The half-life of a reaction: (t_{1/2})

"The time at which the concentration of a reactant to reduce to half of its initial concentration".

Derivation of half-life for zero order reaction <u>Or</u> Show that half-life for zero order reaction is directly proportional to initial concentration of the reactant.

$$t = t_{\frac{1}{2}} \text{ when } [R] = \frac{\left[R\right]_{0}}{2}$$

We know that
$$k = \frac{\left[R\right]_{0} - \left[R\right]}{t}$$
$$k = \frac{\left[R\right]_{0} - \frac{\left[R\right]_{0}}{2}}{t_{\frac{1}{2}}}$$
$$t_{\frac{1}{2}} = \frac{\left[R\right]_{0}}{2k} \quad \text{or} \quad t_{\frac{1}{2}} \propto [R]_{0}$$

Half-life for zero order reaction is directly proportional to initial concentration of the reactant.

Derivation of half-life for first order reaction <u>Or</u> Show that half-life of a first order reaction is independent of the initial concentration:

$$t = t_{\frac{1}{2}} \text{ when } [R] = \frac{\left[\frac{R}{2}\right]_{0}}{2}$$

We know that $k = \frac{2.303}{t} \log \frac{\left[\frac{R}{2}\right]_{0}}{\left[\frac{R}{2}\right]}$
 $k = \frac{2.303}{t_{\frac{1}{2}}} \log \frac{\left[\frac{R}{2}\right]_{0}}{\frac{\left[\frac{R}{2}\right]_{0}}{2}}$
 $t_{\frac{1}{2}} = \frac{2.303 \times \log 2}{k}$
 $= \frac{2.303 \times 0.3010}{k}$
 $t_{\frac{1}{2}} = \frac{0.693}{k}$

➤ Half-life of the first order reaction is independent of the initial concentration.

<u>Pseudo first order reaction:</u> "A reaction of higher order can be converted into first order by altering the reaction conditions" is called **pseudo first order reaction**.

Example: Inversion of cane sugar (Sucrose):

 $\begin{array}{cc} C_{12}H_{22}O_{11}+H_2O \ (excess) & \stackrel{H^+}{\longrightarrow} C_6H_{12}O_6 & + C_6H_{12}O_6 \\ Sucrose & Glucose & Fructose \end{array}$

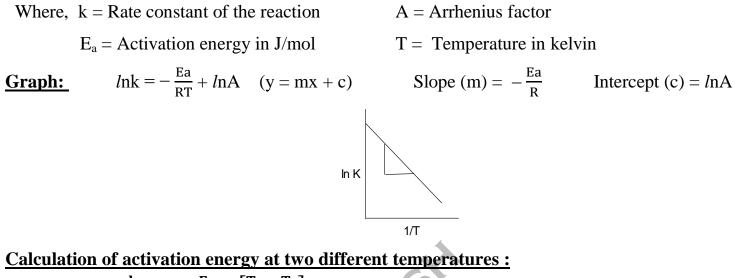
Temperature dependence of the rate of reaction:

- Rate of the chemical reactions increases with increases in temperature.
- > For every 10K (10°C) rise in temperature, rate of reaction get doubled.
- The ratio of rate constant of a reaction at (T + 10)⁰C to the rate constant at T⁰C is called 'temperature coefficient'.
- "The minimum energy that the reactant molecules should posses to form products upon effective collisions" is called **threshold energy**.
- > Energy required to form activated complex is called **Activation energy**.
- The collisions between molecules with the sufficient kinetic energy and proper orientation are called effective collisions.

Arrhenius equation:

This equation gives the relationship beteen Rate contant(k), Temperature(T) and Activation $energy(E_a)$.

$$k = A e^{-\frac{E_a}{RT}}$$



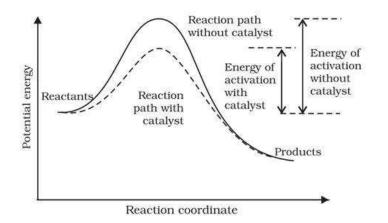
$$\log \frac{k_2}{k_1} = \frac{Ea}{2.303R} \left[\frac{T_2 - T_1}{T_1 T_2} \right]$$
 Using this equation, we can solve for E_a.

(R = 8.314 J/mol/K)

<u>Catalyst:</u> A substance which alters the rate of a reaction without undergoing any chemical change during the reaction.

Effect of catalyst on rate of reaction:

In the reaction, catalyst provides an alternate path with lower activation energy (E_a) for the reaction. Hence the rate of reaction increases in the presence of catalyst.



Important Points:

- \checkmark Catalyst decrease the activation energy of the reaction.
- ✓ Catalyst alters the activation energy, threshold energy, rate of reaction, rate constant and path of the reaction.
- ✓ Catalyst does not alter Gibbs free energy (ΔG), ΔS , ΔH , equilibrium constant, energy of reactants and products.
- ✓ In case of reversible reactions, the catalyst lowers the activation energies of both forward and backward reactions to the same extent and helps in attaining the equilibrium quickly.
- ✓ It catalyzes the spontaneous reactions but does not catalyze non- spontaneous reaction.

Collision theory of chemical reactions:

- Conditions or criteria for effective collisions between reactant molecules:
 a) Proper orientation
 b) Sufficient kinetic energy (threshold energy)
- *Collision frequency:* The number of collisions per second per unit volume of the reaction mixture.
- For bimolecular elementary reaction, $A + B \rightarrow \text{products}$ Rate of reaction can be expressed as, $Rate = PZ_{AB} e^{-Ea/RT}$ Where, P = probability factor or steric factor Z = Collision frequency $E_a = \text{Activation energy}$ T = Absolute Temperature R = Universal Gas constant

Unit-04: d and f block elements

<u>**3d** – series elements:</u> General electronic configuration $[Ar]^{18} 3d^{1-10} 4s^{1-2}$

Exceptional electronic configuration:

- Chromium (Cr) 24: [Ar] 3d⁵ 4s¹ (due to extra stability of completely half filled (d⁵) electronic configuration).
- Copper (Cu) 29: [Ar] 3d¹⁰ 4s¹ (due to extra stability of completely filled (d¹⁰) electronic configuration).
- > Zn, Cd, Hg are non-transition elements (due to completely filled d^{10} electronic configuration).

Variable oxidation states: All transitions elements show variable oxidation states because, of small energy difference between (n-1) d and ns orbitals the electrons present in both (n-1)d and ns orbitals are involved in bond formation.

- \rightarrow The most common oxidation state of 3d series elements is +2.
- \rightarrow *Scandium* do not shows the variable oxidation state.
- \rightarrow In 3d series, *Manganese (Mn)* shows a maximum oxidation state of + 7.
- \rightarrow Example for amphoteric oxides: Cr₂O₃, V₂O₅

Formation of coloured ions:

The colour of the transition metal compounds due to presence of unpaired electrons, which undergo d-d transition by absorbing the energy from visible region.

In the presence of ligand, the degenerated d-orbitals are split up into two sets of orbitals (t_{2g}, e_g) having different energies, is called "Crystal field splitting".

Magnetic property:

- Magnetic property of transition metals / ions is mainly *due to presence of unpaired electrons*.
- Spin only formula to calculate the magnetic moment (μ) is $\mu = \sqrt{n(n+2)} BM$ n = number of unpaired electrons

Catalytic property:

Transition metals and their compounds used as catalysts because they have,

> Tendency to show variable oxidation states.

- \blacktriangleright Tendency to lowering the activation energy by weakening the bonds.
- > Tendency to form reactive intermediates with reactants.

Formation of Complex (or) Co-ordination compounds:

Transition metals form complexes mainly due to,

- \blacktriangleright Presence of vacant d-orbitals.
- → Higher polarizing power (High charge and small size)

Interstitial compounds: The compounds which are formed when small atoms like H, B, N, C are

trapped inside the crystal lattice of metals. **Ex:** Titanium carbide – TiC

Transition metals forms interstitial compounds because

- ✤ Presence of space between metal atoms in their crystal lattice.
- Tendency to shows variable oxidation states.

Characteristics of interstitial compounds:

- \checkmark They have high melting point compare to pure metals. EFS
- \checkmark They retain their metallic conductivity.
- \checkmark They are chemically inert.
- \checkmark They are hard and denser.

Alloy formation: An alloy is a homogeneous solid solution in which atoms of one metal distributed randomly among the atoms of the other.

- > Transition metals forms alloys among themselves because they have similar atomic radii.
- ▶ Alloys of transition metals with non-transition metals are Brass (Cu + Zn) and Bronze (Cu + Sn).

Disproportionation of an oxidation state: The oxidation state is said to be under go

disproportionation when it is less stable relative to other oxidation states one is lower, one higher.

Ex: $Cu^{+1} \rightarrow Cu + Cu^{+2}$

Variation of atomic and ionic sizes (radii):

- ▶ In the beginning (Sc to Cr) atomic and ionic sizes decreases because of increasing in effective nuclear charge (ENC).
- From Mn to Cu, atomic and ionic size almost constant because increase in screening effect balanced by increased ENC.

Towards end, atomic and ionic size increases, because of inter electronic repulsions, electron cloud slightly expands. Hence size increases.

Melting point, boiling point and enthalpy of atomization:

• The melting and boiling points of the transition metals are maximum at the middle of each series.

Reason: Due to the presence of more number of unpaired electrons in the middle of each series, metallic bonding between the atoms is very strong. Therefore they have high melting and boiling points.

• Enthalpy of atomization is maximum in the middle of each transition series.

Reason: Due to the more number of unpaired electrons in the middle of each series, interatomic interaction is stronger. Therefore, enthalpy of atomization is maximum in the middle of each transition series

• Enthalpy of atomization is more in 4d and 5d series than 3d series.

Reason: This is due to the strong metal-metal bonding in 4d and 5d series elements than 3d series elements.

Action of heat on KMnO4:

KMnO₄ decomposed at 513K gives potassium manganate, manganese dioxide and oxygen.

$$2KMnO_4 \xrightarrow{513K} K_2MnO_4 + MnO_2 + O_{2(g)}$$

The lanthanoids (4f – block elements) and Actinoids (5f – block elements):

The lanthanoids are those elements in which differentiating electron enters the anti-penultimate 4f sub shell.

General electronic configuration of lanthanides is $[Xe]^{54} 4 f^{1-14} 5d^{0-1} 6s^2$

- ⇒ Actinides are those elements in which differentiating electron enters the anti-penultimate 5f- sub shell.
- \Rightarrow General electronic configuration of actinides is [Rn]⁸⁶ 5f ¹⁻¹⁴ 6d ⁰⁻¹ 7s²
- \Rightarrow All actinides are **radioactive elements**.
- \Rightarrow Radioactive lanthanide is **Promethium (Pm**).
- \Rightarrow An element with atomic number 100 is **Fermium (Fm).**

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| Cerium | Ce | 58 | $[Xe]4f^1 5d^1 6s^2$ |
|------------|------------------|----|----------------------|
| Gadolinium | Gd | 64 | $[Xe]4f^7 5d^1 6s^2$ |
| | Gd ⁺³ | | [Xe]4f ⁷ |

Oxidation states:

The common oxidation state of lanthanoids and actinoids is $+3^{\circ}$.

- > The stable oxidation state of cerium in aqueous solution is +3.
- Actinides shows more oxidation states compare to lanthanides due to *comparable energies* between 5f, 6d and 7s levels.
- Cerium does not exist +4 oxidation state in aqueous solution.

<u>Reason</u>: Because Ce^{+4} is strong oxidizing agent, it can easily reduce to Ce^{+3} [E⁰ value Ce^{+4}/Ce^{+3} is +1.74V].

Lanthanoid contraction: The gradual decreasing in the size of lanthanides with increasing in atomic number.

Cause of lanthanoid contraction: "Poor shielding of inner 4f electrons".

Consequences of lanthanoid contraction:

> Radii of the elements belonging to same group of 2^{nd} and 3^{rd} transition series is same.

Ex: Zr and Hf has same size. Nb and Ta has same size.

> Separation of lanthanide ions from their mixture become difficult.

Actinoide contraction: The gradual decreasing in the size of actinides with increasing in atomic number.

Causes for actinoid contraction: Poor shielding of 5f electrons.

- \Rightarrow Actinide contraction is greater from one element to another than lanthanide contraction due to poor shielding of 5f electrons in actinoides than 4f electrons in lanthanides.
- ⇒ Actinides are more reactive than lanthanide because in actinoids 5f electrons will be more effectively shielded from the nuclear charge than the 4f electrons of the corresponding lanthanides hence the outer 5f electrons are less firmly held and are available for bonding.
- \Rightarrow Chemistry of actinoids more complicated compare to lanthanoids. Because
 - 1) Actinoids are radio active in nature.
 - 2) Actinoids have greater range of oxidation states compare to lanthanoids.

| Differences between | | |
|--|--|--|
| Lanthanoids | Actinoids | |
| Electrons enters into 4f orbitals. | Electrons enters into 5f orbitals. | |
| Maximum oxidation state is +4. | Maximum oxidation state up to +7. | |
| 4f electrons have greater shielding effect. | 5f electrons have poor shielding effect. | |
| Lanthanide contraction is lesser. | Actinide contraction is greater. | |
| Except promethium, all are non- radioactive. | All are radioactive. | |



Unit-05: Coordination compounds

Postulates (or) Assumptions of Werner theory of coordination compounds:

- In co-ordination compounds, the central metal atom possess two types of valences i.e.,
 a) Primary valence
 b) Secondary valence
- 2) Primary valence is ionisable, variable and corresponds to oxidation state of central metal atom.
- 3) Secondary valence is non-ionisable, non-variable and corresponds to co-ordination number of central metal atom.
- Primary valence satisfied by negative ions, secondary valence satisfied by negative (or) neutral molecules.
- 5) Primary valence is non-directional, secondary valence is directional.

Differences between double salt and complex salts (co-ordination compounds):

| Double salt | Complex salt |
|--|--|
| It loses its identity in solution. | It retains its identity in solution. |
| It does not contain co-ordinate bonds. | It contains co-ordinate bonds. |
| It is stable in solid state. | It is stable in solid state and in aqueous solution. |
| | |

Homoleptic and Heteroleptic complexes:

Complex in which central metal ion attached to one kind of ligands, called homoleptic complex. **Ex:** [Ni(CO)₄]

Complex in which central metal ion attached to more than one kind of ligands called heteroleptic complex. Ex: $[PtCl_2(NH_3)_2]$

Ambidentate ligand: A mono dentate ligand which has two different donor atoms and either of two ligates in the complex.

```
The co-ordination compounds containing ambidentate ligands shows the 'linkage isomerism'. Ex: CN^-, NO_2^-, SCN^-
```

<u>Chelating ligand:</u> A bidentate (or) polydentate ligand which can attach to central metal ion through two (or) more donor atoms is called chelating ligand. **Ex:** EDTA

Denticity of the ligand: The number of ligating groups in a ligand is called denticity of the ligand.

- \Rightarrow **Co-ordination number of central metal ion:** The number of co-ordinate bonds between the ligands and central metal atom / ion in a complex is called as co-ordination number.
- \Rightarrow **Spectrochemical series:** The series of ligands arranged in increasing order of their field strength to split the d-orbitals is called spectrochemical series.

| Ligands | Definition | Examples |
|---------------------|--|--|
| Monodentate ligands | The ligands which can donate only | H ₂ O. NH ₃ , CO (Neutral) |
| | one lone pair of electrons to the | CN^{-} , Cl^{-} , Br^{-} etc. (Negatively |
| | central metal ion. | charged) |
| Di or Bidentate | The ligands which can donate two | Ethylene diamine (Neutral) |
| ligands | pair of electrons to the central metal | Oxalate ion (Negatively charged) |
| | ion. | |
| Hexadentate ligands | The ligands which can donate six pair | EDTA |
| | of electrons to the central metal ion. | |

Structural isomerism in complexes:

i) Ionisation isomerism: Isomers which gives different ions on ionization in water called ionization isomers and phenomenon is called ionisation isomerism.

<u>Ex:</u> [Pt $(NH_3)_4Cl_2$] Br₂ and [Pt $(NH_3)_4Br_2$] Cl₂

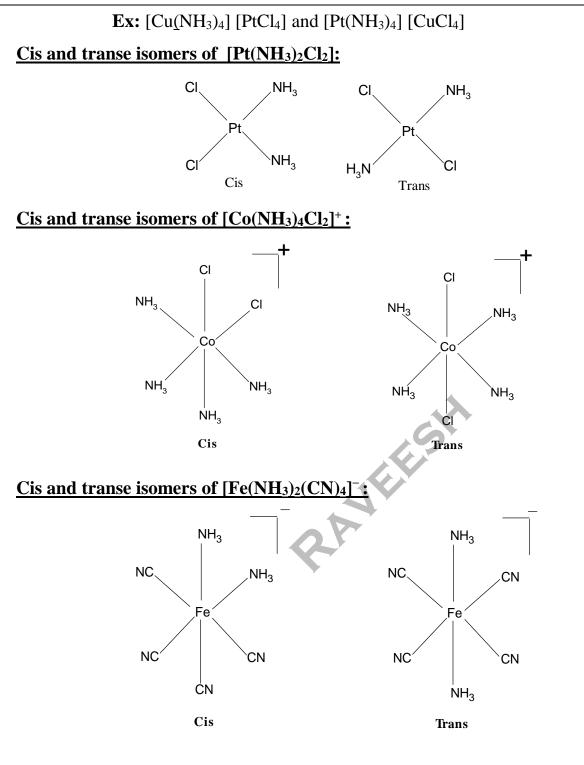
ii) Linkage isomerism: Isomers differ in the mode of attachment of mono dentate ligands(ambidentate ligands) with central metal ion called linkage isomers and phenomenon is calledlinkage isomerism.Ex: $[Co(NH_3)_5NO_2]Cl_2$ and $[Co(NH_3)_5ONO]Cl_2$

Linkage isomerism arises when *ambidentate ligands* such as NO_2^- , CN^- , SCN^- present in co-ordination compounds.

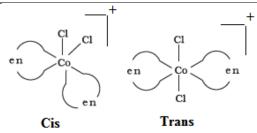
iii) Hydrate (solvate) isomerism: Isomers which differ in the number of water molecules in coordination sphere called hydrate isomers and phenomenon is called **hydrate isomerism**.

Ex: $[Cr(H_2O)_5Cl]Cl_2.H_2O$ and $[Cr(H_2O)_4Cl_2]Cl_2H_2O$

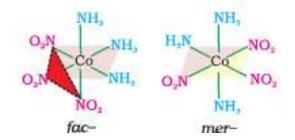
iv) **Co-ordinate isomerism**: This isomerism arises due to the interchange of ligands in the coordination sphere of cationic and anionic parts of complex.



Cis and transe isomers of [Co(en)₂Cl₂]⁺:

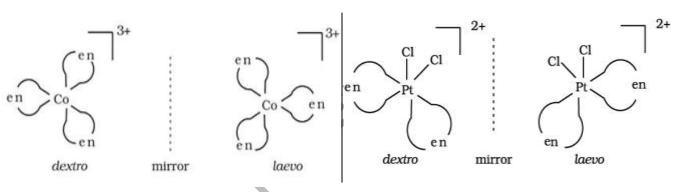


Facial and meridional isomers of [Co(NH₃)₃(NO₂)₃]:

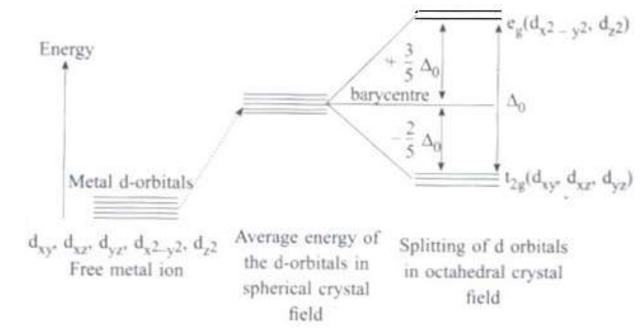


Optical isomers (d and l) of [Co(en)₃]⁺³:

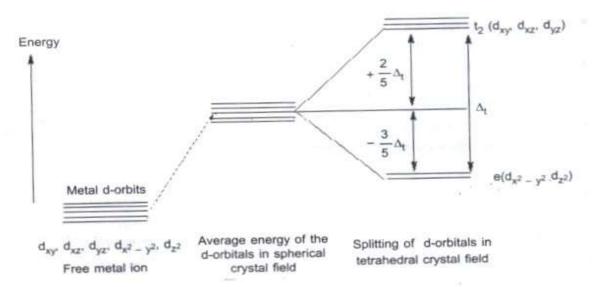
Optical isomers (d and l) of [PtCl₂(en)₂]⁺²:



Crystal field splitting of degenerated d-orbitals in octahedral complexes:



Crystal field splitting of degenerated d-orbitals in tetrahedral complexes:



Importance and applications of co-ordination compounds:

- Cis-platin used in treatment of cancer.
- Hemoglobin is Fe⁺² complex present in blood responsible for transport of O₂ and CO₂ throughout the body.
- > The ligand EDTA⁻⁴ used to determine the hardness of water.
- \blacktriangleright Ni⁺² ion is estimated gravimetrically by complexing with dmg (dimethylglyoxime).
- ▶ [RhCl(pph₃)₃] is called *Wilkinson's catalyst* used for selective hydrogenation of alkenes.
- Extraction of gold and silver through the formation of cyanide complex.
- > In Mond's process, impure Ni is purified by converting into $[Ni(CO)_4]$ complex.

Metal carbonyls:

Metal carbonyls are the organometallic compounds in which ligand is carbon monoxide (CO).

Bonding in metal carbonyls: In metal carbonyls, the metal- carbon have both σ and π character.

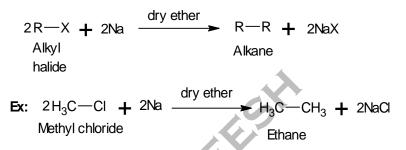
- > M–C σ bond is formed by donation of pair of electrons of carbonyl carbon to the vacant orbital of the metal.
- > M–C π bond is formed by donation of pair of electrons from the filled d orbitals of metal to the vacant antibonding π^* orbital of carbonyl group.
- > The effect of σ bond formation strengthens the π bond and vice- versa. This is called *synergic effect.*

Unit-6: Haloalkanes and Haloarenes

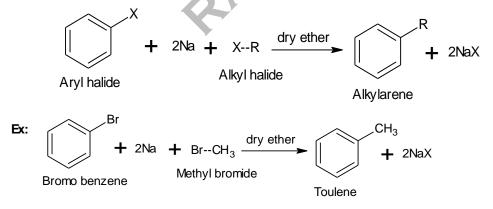
Finkelstein reaction: Alkyl chloride or alkyl bromide on heating with sodium iodide in dry acetone gives alkyl iodide. This reaction is called Finkelstein's reaction.

 $R - X + NaI \xrightarrow{dry acetone} R - I + NaX$ Where, X = Cl, Br

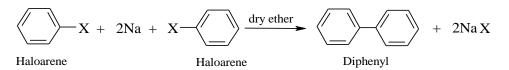
- Swarts reaction: Alkyl chloride or alkyl bromide on heating with AgF / CoF₃ / Hg₂F₂ / SbF₃ gives alkyl fluoride. This reaction is called Swarts reaction.
 - *Ex:* $CH_3 Cl + AgF \longrightarrow CH_3 F + AgCl$ methyl chloride methyl fluoride
- Wurtz reaction: When alkyl halides heated with sodium metal in presence of dry ether gives higher alkane. This reaction is called *Wurtz reaction*.



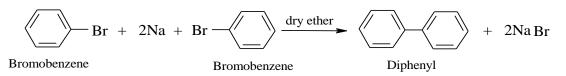
Wurtz-Fittig reaction: When the mixture of aryl halide and alkyl halide treated with sodium metal in dry ether gives alkylarene. This reaction is called *Wurtz-Fittig reaction*.



Fittig reaction: Aryl halides reacts with sodium metal in dry ether to give Diphenyl. This reaction is called *Fittig reaction*.

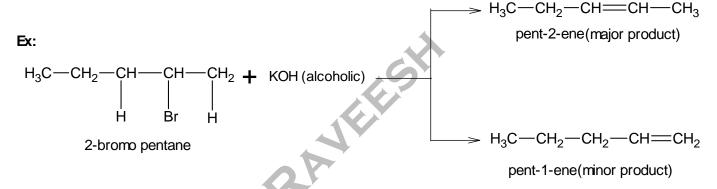


Ex:



Dehydrohalogenation: Alkyl halide containing beta hydrogen undergo elimination reaction in presence of alcoholic KOH gives alkene. This reaction is called dehydrohalogenation.

- During dehydrohalogenation hydrogen is removed from beta carbon atom in alkyl halides. Hence the reaction is called *beta elimination reaction*.
- Reagent used for dehydrohalogenation is Alcoholic KOH (Alcoholic potash).
- Saytzeff's rule: "In dehydrohalogenation reactions, preferred product is alkene which has greater number of alkyl groups attached to the doubly bonded carbon atoms.



Halo arenes (Aryl halides) are extremely less reactive towards nucleophilic substitution reactions due to following reasons:

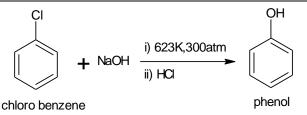
- In haloarenes, due to resonance, C-X bond acquires double bond character. Hence bond strength increases. So difficult to break down the C-X bond.
- Due to instability of phenyl carbocation formed after self-ionization and therefore S_N¹ mechanism rules out.
- > Benzene ring is electron rich so nucleophile cannot attack it easily due to repulsion.

Nucleophilic substitution reactions of alkyl halides:

 $R-X + KCN \rightarrow R-CN + KX \qquad \qquad R-X + AgCN \rightarrow R-NC + KX$

 $R-X + AgNO_2 \rightarrow R-NO_2 + AgX \qquad R-X + KNO_2 \rightarrow R-ONO + KX$

<u>Conversion of chlorobenzene to phenol:</u> Chloro benzene reacts with sodium hydroxide at 623K and 300atm pressure followed by acidification gives phenol.



> <u>Chiral carbon atom or Asymmetric carbon atom or Chirality centre or Stereo centre:</u>

A carbon atom bonded to four different atoms or groups is called chiral carbon atom.

Chiral molecules: The molecules which are non-super imposable on their mirror images are called chiral molecules.

<u>Achiral molecules</u>: The molecules which are super imposable on their mirror images are called achiral molecules.

Chirality: The property of molecules which are non-super imposable on their mirror images.

Condition for molecule to said to be as chiral molecule: Molecule should contain chiral carbon.

Optically active compounds: The compounds which rotate the plane polarized light when it is passed through its solution are called optically active compounds.

Optical activity: The property of compound to rotate the plane polarized light when it is passed through its solution is called optical activity.

<u>Condition for optical isomerism</u>: Compound should not be contain plane of symmetry.

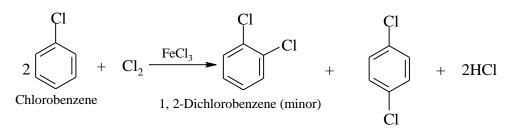
Racemic mixture or Racemic modification:

Equimolar mixture of d and l isomers of same compound is called racemic mixture.

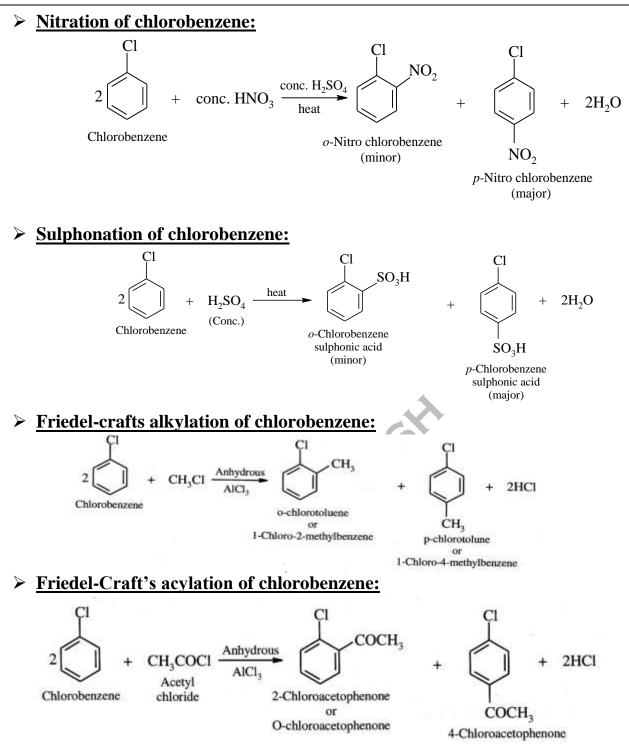
<u>Racemic mixture is optically inactive</u>, because the optical rotation produced by *d*-isomer is cancelled with optical rotation produced by *l*-isomer.

Racemisation: The process of conversion of enantiomer into a racemic mixture.

> <u>Halogenation (Chlorination) of chlorobenzene:</u>



1, 4-Dichlorobenzene (major)



Freons: Chlorofluoro compounds of methane and ethane are called Freons.

When chloroform exposed to sunlight & air it slowly undergoes oxidation forming poisonous gas *phosgene* (*carbonyl chloride*).

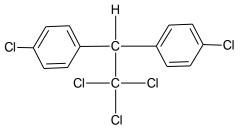
Hence, chloroform is stored in dark coloured bottles which are completely filled without air gap.

DDT (p, p¹-dichloro diphenyl trichloro ethane):

* It is first chlorinated organic insecticide.

Drawback of DDT: It is non-biodegradable, chemically stable and fat soluble.

Structure of DDT:



Unit-7: Alcohols, Phenols and Ethers

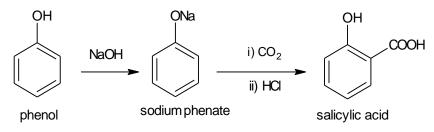
Distinguishing or identification of primary, secondary and tertiary alcohols by Lucas test:

Lucas reagent: Mixture of anhydrous zinc chloride (*ZnCl*₂) *and concentrated hydrochloric acid* (*HCl*)

| Test | Observation | Inference |
|---------------------------|-----------------------------------|------------------|
| Alcohol + Con. HCl | Turbidity appears immediately | Tertiary alcohol |
| + Anhydrous $ZnCl_2$ in a | Turbidity appears after five | Secondary |
| test tube. | minutes | alcohol |
| | Turbidity appears only on heating | Primary alcohol |

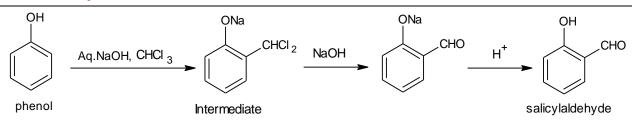
Kolbe's reaction: (Conversion of phenol to salicylic acid):

Sodium phenate heated with carbon dioxide followed by acidification gives salicylic acid. Thos reaction is called Kolbes's reaction.

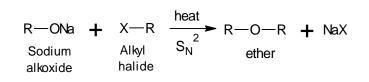


<u>**Riemer – Tiemann's reaction:**</u> Phenol treated with chloroform (CHCl₃) in the presence of sodium hydroxide, followed by hydrolysis gives salicyladehyde.

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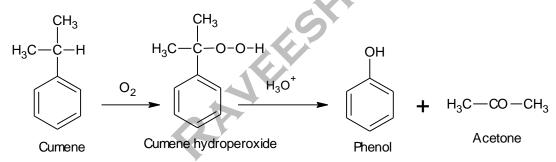


<u>Williamson's synthesis</u>: When sodium alkoxide is heated with alkyl halide, ether is formed. This reaction is called Williamson's ether synthesis. This reaction takes place by S_N^2 mechanism.



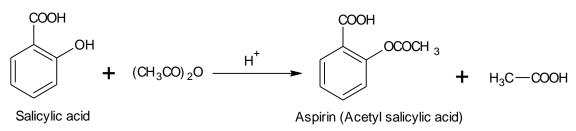
Ex: H_3C —ONa + I— CH_3 \xrightarrow{heat} H_3C —O— CH_3 + NalSodium methyl S_N dimethyl ether methoxide iodide

<u>Cumene process:</u> Preparation of phenol from Cumene (Isopropyl benzene).



Conversion of salicylic acid to aspirin:

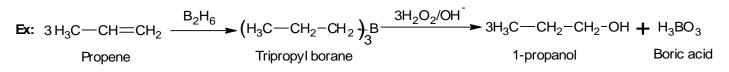
Salicylic acid treated with acetic anhydride in presence of con. H_2SO_4 gives aspirin, reaction is called acetylation.



Hydroboration-oxidation reaction:

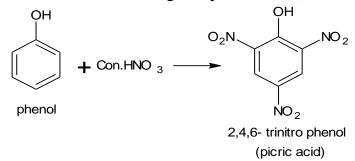
Alkenes react with diborane to give trialkyl borane, which on oxidation using hydrogen peroxide in alkali gives alcohol. This reaction is called *hydroboration –oxidation*.

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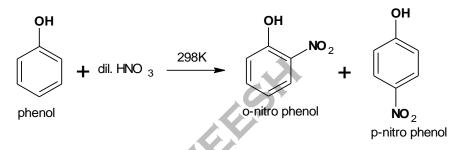


Nitration of phenol:

Phenol treated with *concentrated nitric acid* gives picric acid (2, 4, 6 – tri nitro phenol).

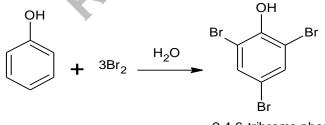


Phenol treated with *dilute nitric acid* at 298K gives mixture of ortho and para nitro phenols.



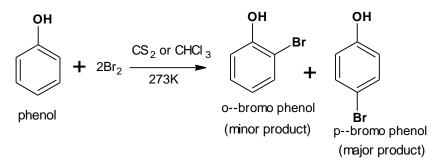
Bromination of phenol :

Phenol reacts with Br_2 water gives white precipitate of 2, 4, 6 - tri bromo phenol.



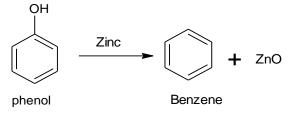
2,4,6-tribromo phenol

Phenol react with *bromine in presence of non-polar solvents like* CS_2 *or* $CHCl_3$ gives ortho and para bromo phenol.

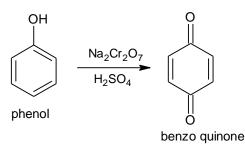


<u>Reaction with zinc dust:</u> Phenol heated with Zn dust gives benzene.

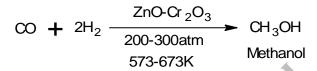
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Oxidation: Phenol undergoes oxidation by chromic acid gives *benzoquinone*.

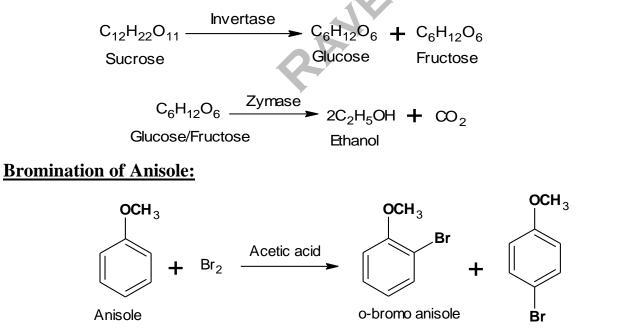


Preparation of methanol:



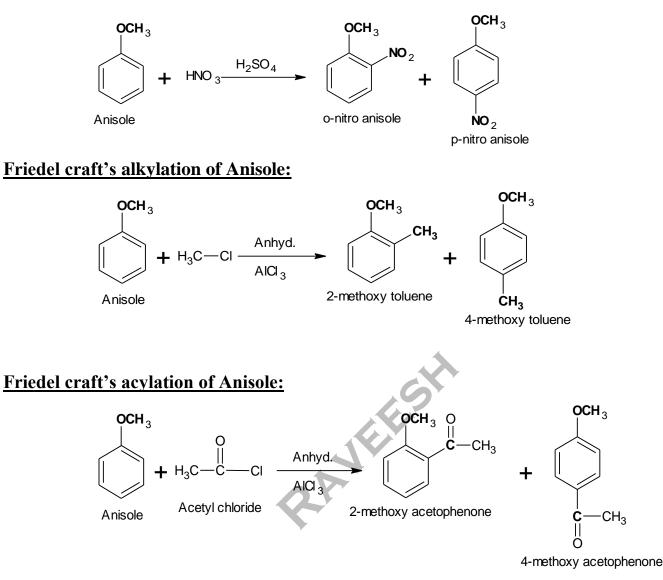
Preparation of ethanol (Fermentation):

Ethanol is prepared by fermentation of molasses by using the enzymes present in yeast.

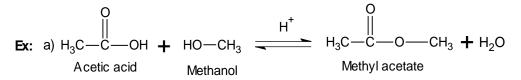


p-bromo anisole

Nitration of Anisole:



Esterification: Alcohols react with carboxylic acids in presence of concentrated H_2SO_4 or dry HCl gives esters. This reaction is called *Esterification*.



Effect of substituent on acidity of phenols:

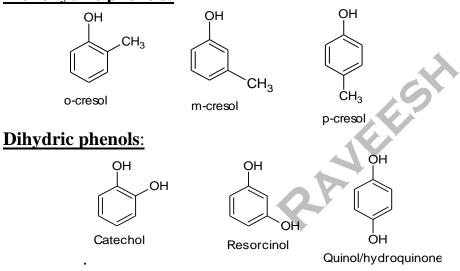
- *a) Electron donating groups like methyl -CH*³ *group*, decreases the acidity of phenols by decreasing the stability of phenoxide ion due to +I effect.
- *b) Electron withdrawing groups like nitro –NO₂ group*, increases the acidity of phenols by increasing the stability of phenoxide ion due to –I effect and –R effect.

Dehydrogenation of alcohols:

- > *Copper* used as dehydrogenating agent.
- Primary alcohol on dehydrogenation gives aldehyde.
- Secondary alcohol on dehydrogenation gives Ketone.
- Tertiary alcohol on do not undergo dehydrogenation. Instead of that they undergo dehydration gives alkene.

Denaturation of alcohol: The commercial alcohol is made unfit for drinking by mixing in it some copper sulphate (to give it a colour) and pyridine (a foul smelling liquid). This process is called as denaturation of alcohols.

Structures of some phenols: Monohydric phenols:



Reasoning type questions:

✓ Phenols are acidic.

<u>Reason</u>: Because phenol dissociate partially to give H^+ ion and phenoxide ion which is stabilized by resonance.

✓ Alcohols are weak acidic than phenols.

Reason: Because in alcohols, the alkoxide ion do not undergo resonance stabilization as like phenoxide ion.

- ✓ The C−O−H bond angle in alcohols is slightly less than tetrahedral angle (109⁰ 28¹).
 Reason: Due to the repulsion between the lone pair electrons on oxygen atom.
- ✓ The C−O−H bond angle in phenol is slightly higher than in alcohols.

Reason: Because lone pair of electrons involved in resonance hence repulsion between lone pair electrons decreases, bond angle increases.

 $\checkmark\,$ The C–O bond length in phenol is less than that of the alcohol.

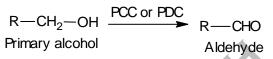
Reason: Because lone pair of electrons in phenol involved in resonance hence C-O bond acquires double bond character. So, C-O bond length decreases in phenols.

✓ The bond angle in ether is higher than tetrahedral angle $(109^0 28^1)$.

Reason: Due to steric repulsion between bulky alkyl groups.

Some important MCQs concepts:

- > Diazonium salt hydrolyzed by warming with water or with dilute acids gives phenol.
- Primary alcohol on oxidation using *pyridinium chloro chromate (PCC) or CrO₃* gives aldehyde.



Secondary alcohol on oxidation using CrO_3 gives ketone.

$$R - HC - R \xrightarrow{CrO_3} R - C - R$$
Secondary alcohol

Secondary alcohol Secondary alcohol When carboxylic acids are reduced by LiAlH₄ primary alcohols are formed.

$$R - COOH \xrightarrow{\text{LiAlH}_4} R - CH_2 - OH$$

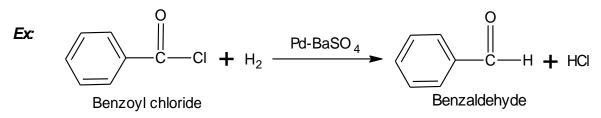
Caboxylic acid Primary alcohol

Unit-8: Carbonyl Compounds

• Hybridization of carbonyl carbon atom is **sp**².

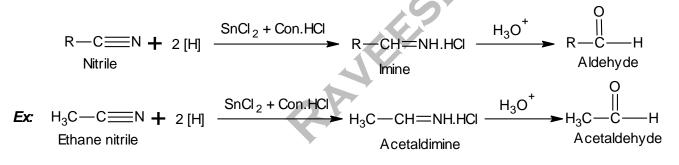
Rosenmund reduction:

Acid (Acyl) chloride reacts with H_2 in the presence of palladium on barium sulphate gives aldehydes. This reaction is called Rosenmund reduction.



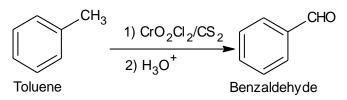
Stephen's reduction:

Nitriles on reduction with stannous chloride (SnCl₂) in presence of Conc.HCl gives imine hydrochloride, which is on hydrolysis gives an aldehyde. This reaction is called Stephen's reduction.



Etard's reaction:

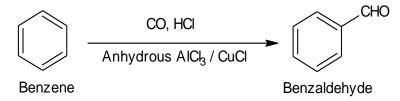
Toluene undergo oxidation with chromyl chloride to a chromium complex, which is on hydrolysis gives benzaldehyde. This reaction is called Etard reaction.



• Oxidizing agent in Etard reaction is *chromyl chloride* (*CrO*₂*Cl*₂).

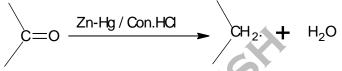
Gatterman-Koch reaction:

Benzene is treated with carbon monoxide and HCl in the presence of anhydrous aluminum chloride or cuprous chloride gives benzaldehyde. This reaction is called Gatterman – Koch reaction.



Clemmensen reduction:

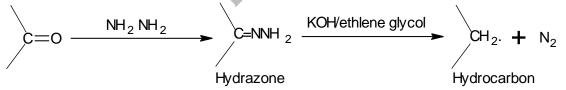
Reduction of -CO- group of aldehyde or ketone to $-CH_2$ – using Zn-Hg and concentrated HCl is called Clemmensen reduction.



• Reagent used in this reaction is Zn-Hg / concentrated HCl.

Wolff-Kishner reduction:

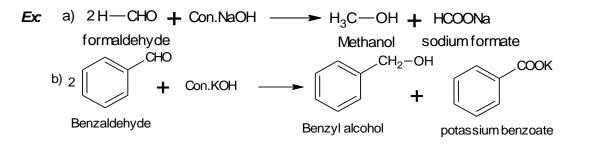
The aldehydes and ketones reacts with hydrazine followed by treating with KOH in ethylene glycol gives hydrocarbons. This reaction is called Wolff-Kishner reduction.



Cannizzaro reaction:

(How formaldehyde or Benzaldehyde does react with concentrated NaOH/KOH?)

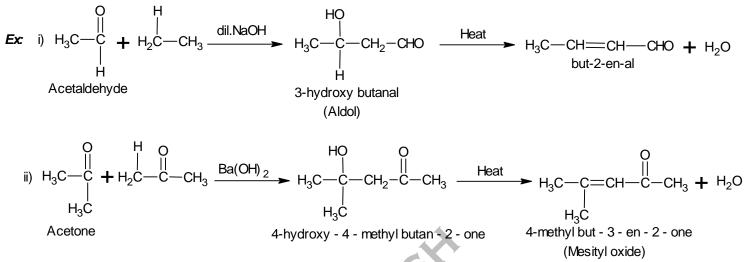
Aldehydes which do not contain α -hydrogen atom are react with concentrated alkali gives a alcohol and a salt of carboxylic acid. This reaction is called Cannizzaro reaction.



Student's Intensifier

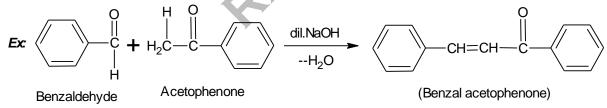
Aldol condensation:

Aldehydes and ketones containing α -hydrogen undergo self-condensation in the presence of dilute alkali to form β -hydroxy aldehyde (aldol) or β -hydroxy ketone (ketol) respectively, which is on heating form α , β -unsaturated aldehydes or ketones with elimination of water. This reaction is called aldol condensation.



Cross aldol condensation or Mixed aldol condensation:

When aldol condensation is carried out between two different aldehydes or different ketones or between an aldehyde and ketone, it is called cross aldol condensation or mixed aldol condensation.



Haloform reaction:

Aldehydes and ketones having *at least one methyl group* linked to the carbonyl carbon atom (methyl ketones) are oxidized by sodium hypohalite to sodium salts of carboxylic acids with one carbon atom less than that of the parent compound. The methyl group is converted to haloform (CHX₃). This reaction is called *halo form reaction*.

$$R - CO - CH_{3} \xrightarrow{\text{NaOX}} R - COONa + CHX_{3} \text{(haloform)}$$

Ex : CH₃ - CO - CH₃ $\xrightarrow{\text{NaOI}}$ CH₃ - COONa + CHI₃
Acetone Iodoform

> Acetaldehyde (Ethanal) is only one aldehyde which gives haloform reaction.

Aldehydes are more reactive than ketones towards nucleophilic addition reactions. Because of following reasons.

- \Rightarrow *Steric effect:* In ketones, presence of two alkyl groups hinders the approach of nucleophile to carbonyl carbon.
- \Rightarrow *Electronic effect:* In ketones, two alkyl groups are reduce the electrophilicity of carbonyl carbon.

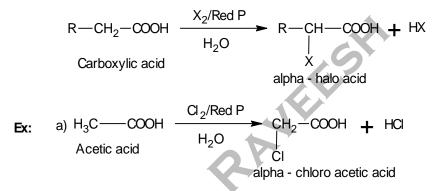
Tollen's reagent: Ammonical silver nitrate solution.

Fehling's solution: Mixture of aqueous copper sulphate and alkaline sodium potassium tartrate.

• Methanal (Formaldehyde) is a gas at room temperature.

Hell–Volhard–Zelinsky reaction or HVZ reaction:

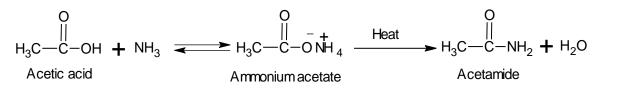
Carboxylic acids with α -hydrogen atom reacts with chlorine or bromine in presence of red phosphorous gives α -halo acids. This reaction is called HVZ reaction.



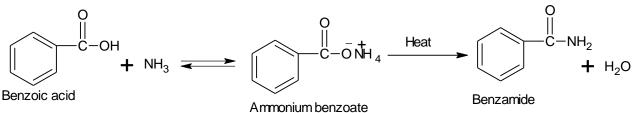
Reaction with ammonia:

Carboxylic acids react with ammonia to form ammonium salts which upon heating lose water molecule to form corresponding amide.

Ex: a) Conversion of acetic acid to acetamide

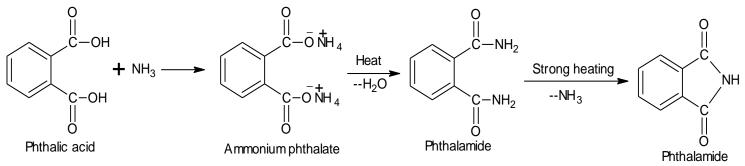


b) Conversion of benzoic acid to benzamide



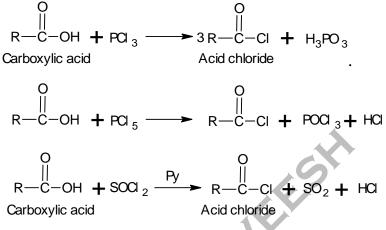
Student's Intensifier

c) Conversion of phthalic acid to phthalimide



Reaction with PCl₃ / PCl₅ / SOCl₂:

➤ Carboxylic acids react with PCl₃/ PCl₅/ SOCl₂ gives corresponding acid chlorides.



Reduction of carboxylic acids:

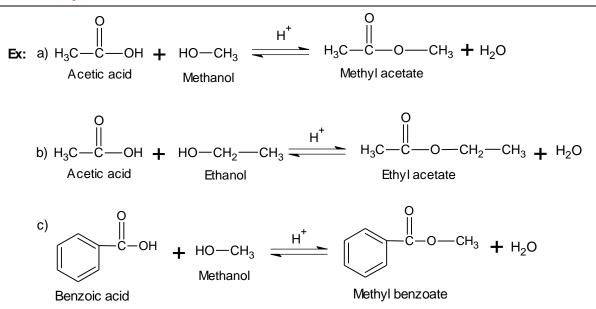
When carboxylic acids are reduced by a strong reducing agent like *LiAlH*₄ or better with *diborane* primary alcohols are formed.

$$R - COOH + 4[H] \xrightarrow{\text{LiAlH}_4} R - CH_2 - OH + H_2O$$

Caboxylic acid alcohol

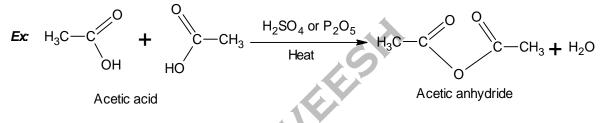
Esterification:

Carboxylic acids react with alcohols in presence of concentrated H_2SO_4 or dry HCl gives esters. This reaction is called Esterification.



Formation of anhydrides:

Carboxylic acids on heating with Con.H₂SO₄ or P₂O₅ gives corresponding anhydrides.



Decarboxylation reaction:

The process of removal of CO_2 from sodium salt of carboxylic acids using dry soda lime is

called decarboxylation gives hydrocarbon.

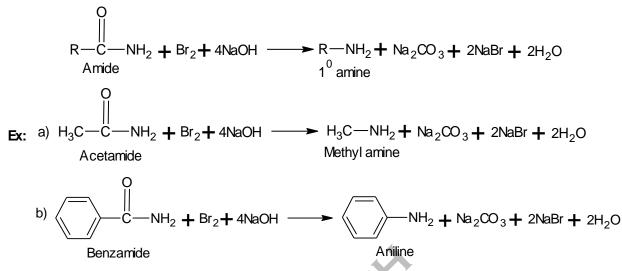
 $R - COONa \xrightarrow{NaOH + CaO} R - H + Na_2CO_3$

• Reagent used for decarboxylation reaction is *sodalime* (*NaOH* + *CaO* in the ratio 3:1).

Unit-9: Organic compounds containing nitrogen

Hoffmann bromamide degradation reaction:

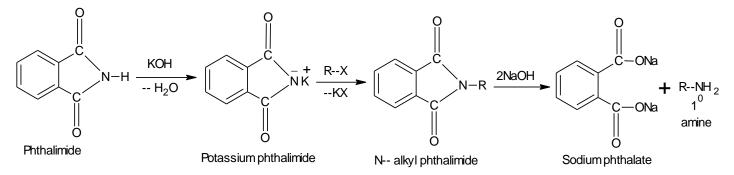
Amides on heating with bromine in aqueous or ethanolic solution of NaOH gives 1°amines. This reaction is called Hoffmann bromamide reaction.



Hoffmann's bromamide reaction is called *degradation reaction*, because product (amine) obtained is containing one carbon atom less than the amide. So it is called <u>degradation</u> <u>reaction</u>.

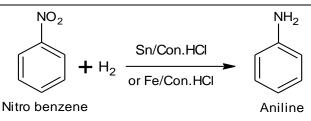
Gabriel phthalimide synthesis:

The potassium phthalimide on heating with alkyl halides followed by alkaline hydrolysis with gives primary amine. This reaction is called



Reduction of nitro compounds:

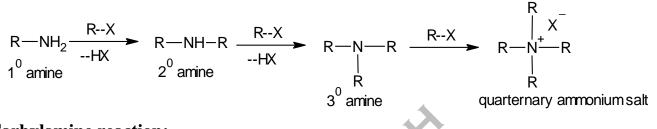
Nitro compounds on reduction using hydrogen in presence of Ni/Pd/Pt catalyst or Sn / Conc. HCl or Fe / Conc.HCl or LiAlH₄ gives primary Amines.



Ammonolysis:

The process of cleavage of the C - X bond of alkyl halides by ammonia is called ammonolysis.

When an alkyl halides reacts with alcoholic ammonia in a sealed tube at 373K gives mixture of 1^0 , 2^0 and 3^0 amines and finally gives the quaternary ammonium salt.



Carbylamine reaction:

When aliphatic and aromatic primary amines are heated with chloroform (CHCl₃) and alcoholic potash (KOH) gives isocyanides (carbylamines). This reaction is called carbylamine reaction.

$$\begin{array}{c} R-NH_{2}+CHO_{3}+3KOH (alcoholic) \xrightarrow{Heat} R-NC + 3KOI + 3H_{2}O \\ 1^{0} \text{ amine} & \text{isocyanide} \end{array}$$

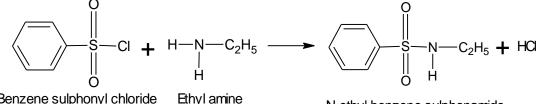
$$Exc \text{ a) } H_{3}C-NH_{2}+CHO_{3}+3KOH (alcoholic) \xrightarrow{Heat} H_{3}C-NC + 3KOI + 3H_{2}O \\ Methyl \text{ amine} & Methyl \text{ isocyanide} \end{array}$$

$$\begin{array}{c} b) & \swarrow \\ NH_{2}+CHO_{3}+3KOH (alcoholic) \xrightarrow{Heat} \sqrt{NC + 3KOI + 3H_{2}O} \\ Methyl \text{ isocyanide} & Methyl \text{ isocyanide} \end{array}$$

Reaction with benzene sulphonyl chloride (Hinsberg's reagent):

Primary and secondary amines reacts with benzene sulphonyl chloride gives sulphonamides. This reaction is used to distinguish 1^0 , 2^0 and 3^0 amines.

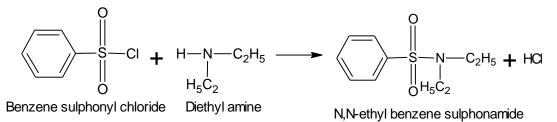
 \Rightarrow Primary amine reacts with benzene sulphonyl chloride to form N-ethyl benzene sulphonamide, which is soluble in alkali.



Benzene sulphonyl chloride

N-ethyl benzene sulphonamide

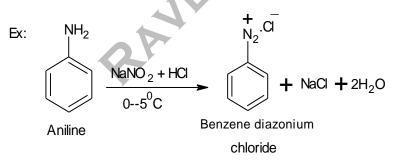
 \Rightarrow Secondary amine reacts with benzene sulphonyl chloride to form N, N- diethyl benzene sulphonamide, which is insoluble in alkali.



 \Rightarrow Tertiary amine does not reacts with benzene sulphonyl chloride due to absence of H-atom on 'N' atom.

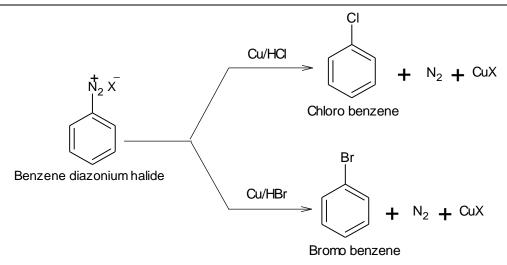
Diazotization reaction:

Aromatic primary amines reacts with nitrous acid at 0-5°C (273-278K) gives benzene diazonium salt. This reaction is called *diazotization reaction*.



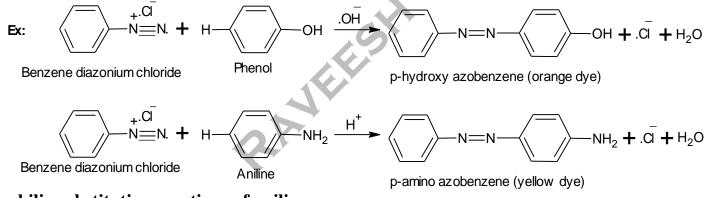
Gatterman reaction:

The process of introducing a halogen atom into an aromatic ring by treating the diazonium salt with corresponding halogen acids in the presence of copper powder is called Gatterman reaction.



Coupling reactions:

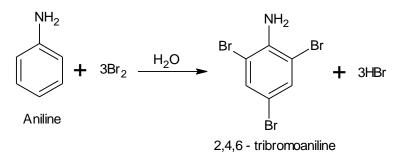
Benzene diazonium chloride reacts with aromatic amines (aniline) in weakly acidic medium or phenol in weakly basic medium to give azo dyes by coupling at ortho or para positions of aniline or phenol. These reactions are called coupling reactions.



Electrphilic substitution reactions of aniline:

Bromination:

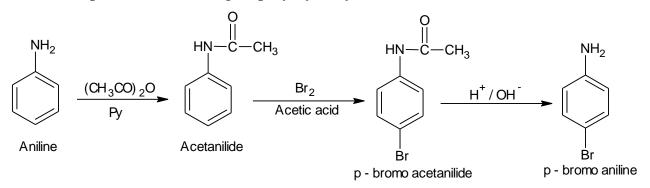
Aniline reacts with bromine water gives white precipitate of 2,4,6-tribromoaniline.



<u>Nitration</u>: Direct nitration of aniline gives mixture of ortho (2%), meta(47%) and para(51%) nitro anilines.

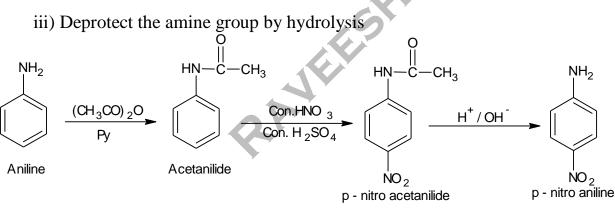
Steps to obtain p-bromo aniline:

- i) Protecting amine group by acetylation with acetyl chloride.
- ii) Bromination.
- iii) Deprotect the amine group by hydrolysis.



Steps to obtain p-nitro aniline:

- i) Protecting amine group by acetylation with acetyl chloride.
- ii) Nitration



Boiling points:

> Amines having higher boiling point compare to corresponding hydrocarbons.

Reason: Due to intermolecular hydrogen bonding in amines.

The order of boiling point of isomeric amines is in the order, 1° amine > 2° amine > 3° amine.

Reason: In *primary amines*, two hydrogen atoms on nitrogen involved in intermolecular hydrogen bonding. In *secondary amines*, only one hydrogen atom on nitrogen involved in intermolecular hydrogen bonding. In *tertiary amine*, no inter molecular hydrogen bonding due to absence of hydrogen atom on nitrogen.

Solubility: Aliphatic amines of lower molecular masses are soluble in water due to *formation of hydrogen bonding with water*.

Basic nature of amines:

Amines are basic in nature due to the presence of lone pair of electrons on nitrogen atom. Hence they behave as *Lewis base*.

Interpretation of basicity of alkyl amines, ammonia, and aniline:

\Rightarrow <u>Alkyl amines are more basic than ammonia.</u>

<u>**Reason**</u>: Due to +I effect of alkyl groups (electron releasing groups), electron density on the nitrogen atom increases and hence easily available for donation.

Ex: Methyl amine more basic than ammonia.

Due to + I effect of -CH₃ group (electron releasing group) electron density on the nitrogen atom increases and hence easily available for donation. Hence it is more basic than ammonia.

\Rightarrow <u>Aniline (Aryl amine) are less basic than ammonia.</u>

Reason: Due to resonance effect in aniline, the electrons present on the 'N' atom involved in resonance with benzene ring.

Variation of basic strength of 1⁰, 2⁰ and 3⁰ amines:

- In gas phase medium or in non-aqueous solvents like chloro benzene basicity order is:
 3° amine > 2° amine > 1° amine
- Based on the +I effect, basicity order is, $3^{\circ} amine > 2^{\circ} amine > 1^{\circ} amine$.
- Based on the steric effect, basicity order is, $1^{\circ} amine > 2^{\circ} amine > 3^{\circ} amine$.
- Based on hydration effect, basicity order is, $1^{\circ} amine > 2^{\circ} amine > 3^{\circ} amine$.
- Basicity of *methyl substituted amines* in aqueous medium is

 $(CH_3)_2NH > CH_3NH_2 > (CH_3)_3N > NH_3$

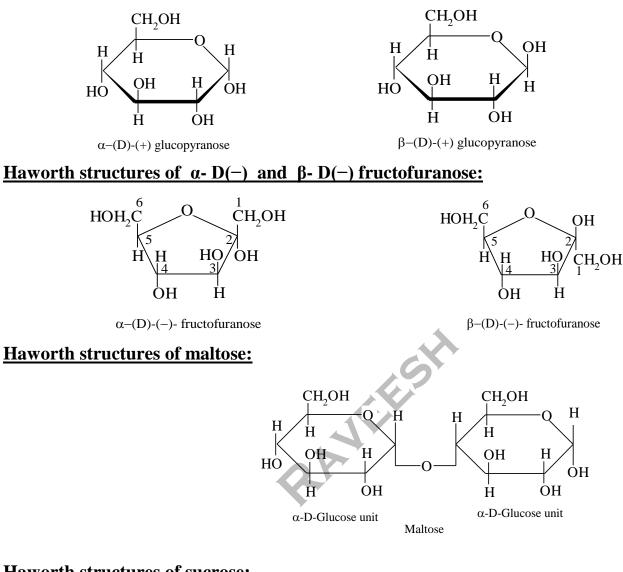
• Basicity of *ethyl substituted amines* in aqueous medium is

 $(C_2H_5)_2NH > (C_2H_5)_3N > (C_2H_5)_2N > NH_3$

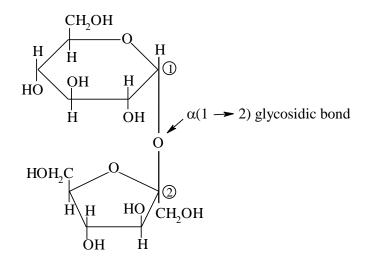
- Basicity $\propto K_b$ value
- Basicity $\propto \frac{1}{p^{K_b}}$ value

Unit-10: Biomolecules

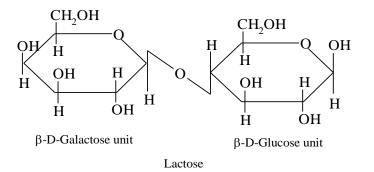
Haworth structures of α - and β - D(+) glucose:



Haworth structures of sucrose:



Haworth structures of lactose:



Structure of elucidation of glucose:

 <u>Reaction with HI:</u> Glucose on heating with hydro iodic acid and red phosphorus undergoes reduction to give *n*-hexane. This reaction indicates the presence of *straight chain of six carbon atoms in* glucose.

$$Glucose + HI \rightarrow n$$
-hexane

2. <u>*Reaction with hydroxyl amine:*</u> Glucose reacts with hydroxyl amine to give glucose oxime and reacts with HCN gives glucose cyanohydrin. This reaction confirms the presence of carbonyl (> C = O) group (aldehyde or ketone) in glucose.

Glucose + HCN \rightarrow glucose cyanohydrin Glucose + NH₂OH \rightarrow glucose oxime

3. <u>Reaction with bromine water:</u> Glucose undergoes oxidation by mild oxidizing agents like bromine water gives *gluconic acid*. This reaction confirms that carbonyl group in glucose is an *aldehyde*.

 $Glucose + Br_2 \text{ water} \rightarrow Gluconic \text{ acid}$

4. <u>*Reaction with acetic anhydride:*</u> Glucose reacts with acetic anhydride to give penta-acetyl glucose (glucose penta acetate). This reaction the presence of *five –OH groups* in glucose.

 $Glucose + (CH_3CO)_2O \rightarrow Glucose penta acetate$

Glucose undergoes oxidation by strong oxidizing agents like nitric acid gives *saccharic acid* (dicarboxylic acid). This reaction confirms the presence of primary alcoholic group.

 $Glucose + Con. HNO_3 \rightarrow Saccharic \ acid$

Reducing sugars and Non-reducing sugars:

✓ The sugars which reduces Tollen's reagent and Fehling's solution are called *reducing* sugars. Ex: Glucose, Fructose, Lactose, and Maltose.

- ✓ The sugars which do not reduces Tollen's reagent and Fehling's solution are called as *non-reducing sugars*. *Ex*: Sucrose
- Sucrose is non-reducing sugar. Why?
 Ans: In sucrose carbonyl group involved in glycosidic linkage and hence not free to reduce Tollen's reagent and Fehling's solution.
- ✓ Storage polysaccharide present in plants *Starch*
- ✓ Storage polysaccharide present in animals *Glycogen*
- ✓ Water soluble components of starch *Amylose*
- ✓ Water insoluble components of starch *Amylopectin*
- ✓ A predominant constitute of cell wall plant cells *Cellulose*
- ✓ Example for aldohexose and dextrose *Glucose*
- ✓ Example for ketohexose *Fructose*
- ✓ Laevorotatory sugar *Fructose*
- ✓ Sugar present in milk *Lactose*
- ✓ Invert sugar *Sucrose*
- ✓ Monosaccharide present in starch a glucose
- ✓ Monosaccharide present in cellulose β *glucose*
- ✓ Animal starch Glycogen

Monosaccharides: Carbohydrates which cannot be hydrolyzed are called monosaccharides.

Ex: Glucose, fructose etc..

<u>Oligosaccharides:</u> Carbohydrates which gives two to ten monosaccharide units on hydrolysis are called oligosaccharides. **Ex:** Maltose, sucrose etc..

ESt

- Maltose on hydrolysis gives two molecules of *glucose*.
- Sucrose on hydrolysis gives *glucose and fructose*.
- Lactose on hydrolysis gives *glucose and galactose*

Polysaccharides: Carbohydrates which gives many monosaccharide units on hydrolysis are called polysaccharides. **Ex:** Starch, Glycogen

Differences between

| Amylose | Amylopectin |
|----------------------------------|------------------------------------|
| 1. Water soluble component. | 1. Water insoluble component. |
| 2. It is a linear chain polymer. | 2. It is a branched chain polymer. |

Proteins:

Denaturation of protein:

The process of loss of biological activity of proteins due to unfolding of globules and uncoiling of helix by changing temperature or pH.

Ex: i) Coagulation of egg white on boiling. ii) Curdling of milk

During denaturation,

- \succ 1° structure remains same.
- \triangleright 2° and 3° structures are destroyed.

Fibrous proteins: These are fibre like proteins in which polypeptide chains are run parallel and held by hydrogen and disulphide bonds.

Ex: Keratin-present in hair, wool, silk, Myosin- present in muscles

Globular proteins: Proteins in which the polypeptide chains are coil around to give spherical

shape. Ex: Insulin, Albumins

Difference between

| Fibrous proteins | Globular proteins |
|---------------------------------|----------------------------|
| They have fibre like structure. | They have spherical shape. |
| Insoluble in water. | Soluble in water. |

Peptide bond: An amide bond formed between two amino acids is called as peptide bond or peptide linkage.

| Type of peptide | Number of amino acid residues | Number of peptide bonds |
|-----------------|-------------------------------|-------------------------|
| Dipeptide | 2 | 1 |
| Tripeptide | 3 | 2 |
| Tetrapeptide | 4 | 3 |
| Pentapeptide | 5 | 4 |
| Polypeptide | N | n-1 |

Student's Intensifier

- > A peptide formed by combining more than 10 amino acids is called *polypeptide*.
- > *Insulin* contains 51 amino acids.

Main forces which stabilize the 2° and 3° structures of proteins:

Hydrogen bonds, Disulphide linkages, Van der Waals and electrostatic forces of attraction.

<u>**Zwitter ion:**</u> The dipolar ion which neither move towards anode nor cathode under the influence of electric field. This ion carries both positive and negative charges.

The general structure of Zwitter ion is,

$$H O H_3N^+ - C - C - O^-$$

Acidic amino acids: Amino acids contain two carboxylic acid groups and one amino group.

Ex: Aspartic acid, Glutamic acid.

Basic amino acids: Amino acids contain two amino groups and one carboxylic acid group.

Ex: Lysine, Histidine, Glutamine

Neutral amino acids: Amino acids contain one amino group and one carboxylic acid group.

Ex: Alanine, Glycine, Serine

Essential amino acids: Amino acids that are not synthesized in the body are called essential amino acids. **Ex:** Valine, Leucine, Isoleucine, Arginine, Methionine, Phenylalanine, Lysine, Threonine, Tryptophan and Histidine.

Non-essential amino acids: Amino acids that are synthesized in the body are called non-essential amino acids. **Ex:** Glycine, alanine, glutamic acid aspartic acid, tyrosine, serine, cysteine, proline, asparagine and glutamine.

Important points:

- ✓ Optically inactive amino acid: *Glycine*
- ✓ Example for aromatic amino acids: *Phenylalanine*, *Tryphtophan*
- ✓ Hetero cyclic amino acids: *Histidine, Proline*
- ✓ Sulphur containing amino acids: *Cysteine, Methionine*
- ✓ Alcoholic amino acids: *Serine*, *Threonine*
- ✓ Phenolic amino acid: *Tyrosine* (containing phenolic −OH)

✓ Imino acid: *Proline*

Nucleic acids:

Complete hydrolysis of DNA or RNA yields a pentose sugar, phosphoric acid and nitrogenous base.

The sugars:

- The sugar present in DNA is β -2-deoxy-D-ribose.
- The sugar present in RNA is β -D-ribose.

The nitrogenous bases:

The nitrogenous bases present in both DNA and RNA - Adenine, Guanine, Cytosine

The nitrogenous bases present in DNA but absent in RNA - Thymine

The nitrogenous bases present in RNA but absent in DNA - Uracil

Nucleoside: A unit formed when nitrogenous base gets attached to 1st position of pentose sugar is called nucleoside.

Nucleotide: When nucleoside is linked to phosphoric acid at 5th position of pentose sugar gives nucleotide.

Nucleotides are joined together by phosphodiester linkage.

Vitamins:Vitamins are organic compounds required in the diet in small amounts to perform specific biological functions for optimum growth and health.

Water-soluble vitamins: 'B' group vitamines and vitamin 'C'

Fat-soluble vitamins: Vitamins A, D, E, and K

Qn: Why cannot vitamin-C be stored in our body?

Ans: Because vitamin-C is water soluble , therefore, it readily excreated in urine.

Qn: Name the water soluble vitamin stored in our body.

Ans: Vitamin B_{12} .

| Name of the Vitamin | Deficiency diseases |
|-----------------------------------|--|
| Vitamin-A | Night blindness and |
| | Xerophthalmia (hardening of cornea of eye) |
| Vitamin B ₁ (Thiamine) | Beri Beri |

| Vitamin B ₂ (Riboflavin) | Cheilosis, digestive disorders | |
|-------------------------------------|---|--|
| Vitamin B ₆ (Pyridoxine) | Convulsions | |
| Vitamin B ₁₂ | Pernicious anaemia (deficiency of RBC) | |
| Vitamin C (Ascorbic acid) | Scurvy (bleeding gums). | |
| | Rickets (bone deformities in children) and | |
| Vitamin D | osteomalacia (soft bones and joint pain in adults). | |
| | Increased fragility of RBC'S and muscular | |
| Vitamin E | weakness. | |
| Vitamin K | Increased blood clotting time. | |

Hormones:

- Intercellular messengers are called hormones.
- Iodine containing hormone *Thyroxine*
- Low level of thyroxine leads to *hypothyroidism*
- High level of thyroxine leads to *hyperthyroidism*

Important types of hormones and their functions:

| Туре | Example | Function |
|----------------------|---|---|
| Polypeptide hormones | 1. Insulin | It decrease blood sugar (glucose) level. |
| | 2. Glucagon | It increase blood sugar (glucose) level. |
| Amino acid | 1. Epinephrine | Increase pulse rate and controls blood |
| derivatives | | pressure. |
| | 2. Thyroxine | Growth and development. |
| Steroid hormones | 1)<u>Adrenal cortex hormones</u> (corticoids): a) Glucocorticoids | Control the carbohydrate metabolism, modulate inflammatory reactions. |
| | | modulate inflammatory reactions. |

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| b) Mineralocortic | coids Control the level of excretion water and |
|-------------------------|---|
| 2) <u>Sex homones</u> . | salt by kidney. |
| a) Testosterone | Responsible for the development of |
| a) resiosierone | secondary male characteristics. |
| b) Estradiol | Responsible for the development of <i>secondary female characteristics</i> and participate in control of menstrual cycle. |
| d) Progesterone | Responsible for preparing the uterus for implantation of fertilized egg. |

> Abnormal function of adrenal cortex causes *Addison's disease*.

